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This problem is a classical one and is described in all general thermodynamic books, so that only some special points need be considered here. The experimental work so far done on the subject has been excellently summarized by L. G. Hoxton,[1] who also gives a good bibliography. E. S. Burnett's work[2] on carbon dioxide should be added to this list.

The experiment consists in allowing air to expand from a known pressure and temperature through some sort of porous partition to some lower pressure, and in measuring the new temperature assumed by the air. This requires a supply of compressed air, the control of initial and final pressures and of initial temperature, and also the measurement of both pressures and both temperatures. The apparatus used for each of these purposes will be described.

The plan adopted for taking the data is the well known[21] one of dropping from a fixed initial temperature and pressure successively to a series of values of the lower pressure and measuring each resulting lower temperature. The series of pressures and temperatures, including the initial values, are thus the same as would be obtained by a succession of thermometers and pressure gauges along an insulated linear plug. Since the process may be made adiabatic to a close approximation, the only exchange of energy possible is through the pv relations. This is usually stated as

$$u + pv = \text{constant} = h$$

where u is the intrinsic energy and pv the volume energy. This quantity $(u + pv)$ has been called the "enthalpy" and these curves "isenthalpic curves" or "isenthalps." The Joule-Thomson coefficient or porous plug coefficient is then

$$\left(\frac{\Delta T}{\Delta p}\right)_h = \mu$$

where h is the enthalpy, and μ is consequently the slope of these curves.

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Work on this problem has been under way in this laboratory since 1905, first by E. S. Burnett and later by the writer. Many things have interfered, and this report is consequently the result of six or seven years of spare time work. The mere maintenance of a complicated set up such as here described consumed considerable of this time.

Thermostat Bath Arrangements.

The apparatus was originally planned by the writer and Mr. Burnett together, and this second construction utilized a number of points which experience had shown to be desirable. It is quite similar to the apparatus used by the writer for porous plug work with water.[3] A vertical cross section of the cylindrical arrangement is shown diagrammatically in Fig. 1. The central part of three superposed cylinders is a single forging of chrom-vanadium steel of the dimensions shown in inches. The outer case is a piece of autogenously welded steel tube which rests on a lead gasket set in grooves at each end and is held in place by screws through riveted-on flanges. The cover is a brass plate held at the center against a lead gasket by a nut running on the central steel tube.

The annular space thus enclosed is divided by a cylinder *aaaa* into two concentric annular spaces. A centrifugal pump *bb* is formed of a group of radial vanes rotating on the steel tube and driven by a gear on a shaft coming down through the cover. The bath liquid is hence forced to circulate through the two annular spaces as indicated by the arrows and the rotation of the pump also serves to displace the fluid continually around the axis. At about 900 r.p.m. the stirring is violent, and the fluid moves rapidly around its path. As a test the kerosene level was set below the top of the flow-dividing cylinder, and under these conditions the stirrer would maintain about 10 cm. difference of level. The bath had to be kept full and the high speed shaft free of protuberances, or air was churned into the fluid and caught by the down flowing column, till the flow almost ceased. An overflow tank was provided.

The compressed air supply entered at *c* in the base. Connections of all kinds were kept off the steel outer case so that it might be easily removed. Inside the bath the air pipe went vertically about half the bath height, then divided into two steel pipes (¼″ inside) wound oppositely in two layers, till at the top they joined each other again and entered the central cylinder at *e*. The coiled pipe in the lower half of the bath was intended for use when working near the saturation

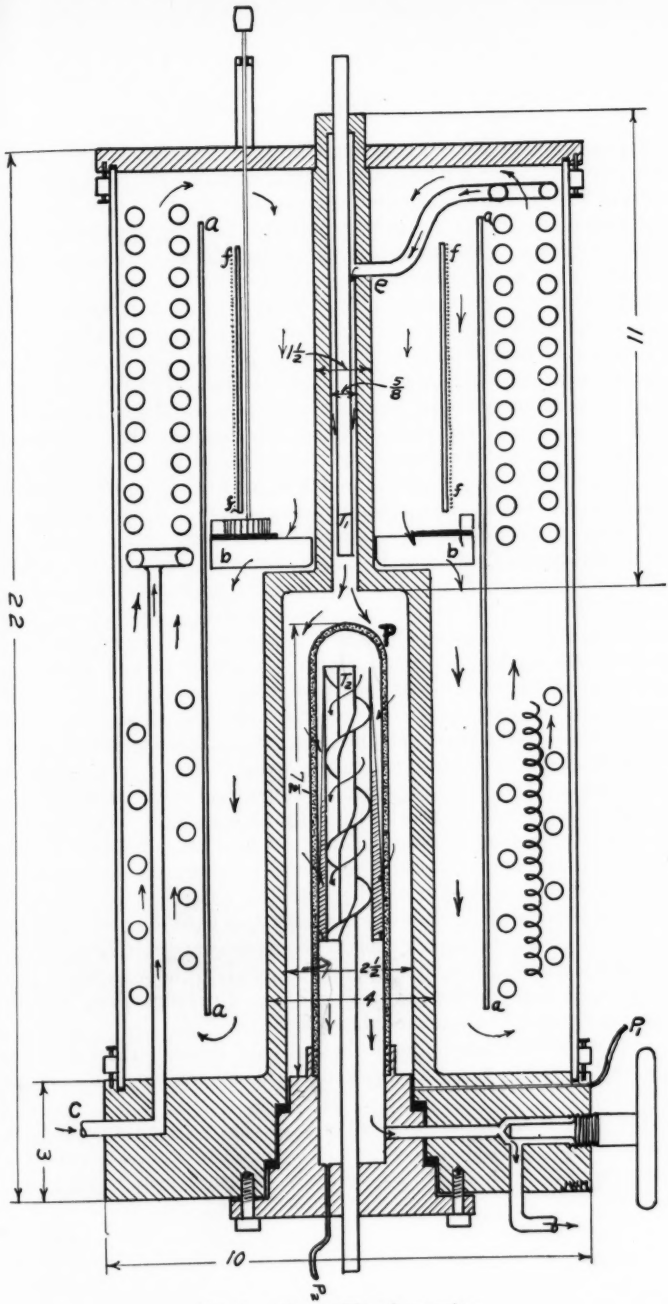

FIG. 1. Porous Plug Apparatus.

conditions. The air after passing through the plug could be passed through this lower coil to bring its temperature back to that of the bath. The valves and connections are all in the base. A complete working drawing makes a very complicated picture, since everything has to be readily demountable to permit the almost continuous series of repairs and modifications such work requires.

The heating elements are placed in between the two layers of the lower coil. They are made of nichrome wire wound on glass tubes supported on brass rods forming part of a frame. The three leads go out through the base through mica insulation. The coils are connected so that the two groups may be used in parallel or in series.

The two thermostat coils of nickel wire are wound on the brass cylinder *ffff*, and the four leads go out the top of the bath. The top of the central cylinder is fitted with a union for holding the thermometer case. The coil of the thermometer is thus in the air just before it enters the plug chamber. In most of the work, a steel spiral flow guide was placed in the annular space (diameters $\frac{3}{8}''$ and $\frac{5}{8}''$) about the thermometer. When difficulty arose at the higher temperature part of the work, this spiral guide was replaced by a thin brass tube into which the thermometer case slipped neatly. Bare copper wire, no. 30, was wound into a coil about $\frac{1}{8}''$ outside diameter and the wires were spaced three or four wire diameters apart. This coil was then wound gently around the brass tube, fluxed, and dipped in molten lead. The result was to fill the annular space about the thermometer, through which the air flows, with a net of heat conducting wire loops. The thermometer then responded much more rapidly to change in air temperature, the difference being quite noticeable in the ordinary routine of observations. In case the outer wall is at a slightly different temperature from the air-flow, the temperature read on the thermometer will be but little influenced by this wall difference—at least to a much less extent than with the previous flow guide. Such an arrangement might be an advantage within the plug, to aid the mixing and averaging, and to speed up the response. The increase of viscous friction, and therefore of pressure drop, would, however, certainly introduce other difficulties.

Two small holes were bored horizontally through the base into the central cavity to serve as pressure leads for the barostat and the manometer.

The plug is supported within the large cavity by another chrom-vanadium steel forging. Contact is made on the double shoulders, each supplied with a lead gasket, and they are held together by

eleven $\frac{3}{4}''$ hard steel bolts. The upper gasket serves to retain the compressed air in the chamber outside the plug and the lower gasket to retain the air at the pressure inside the plug and so to force it over into the base proper and to the valve in the line there. This valve was used for restricting the out-flow and raising the pressure inside the plug to the desired value. To require two gaskets to come tight independently is usually not a good arrangement. Here the lead was compressed very severely by the bolts and was retained by good fitting joints. Both sides of the joints being of the same metal, temperature changes did not spoil the tightness. Very small leaks were of no moment for the present purpose, and noticeable leakages gave only a small amount of trouble. A coat of graphite in oil made everything come apart readily after being at the high temperature. All the oil evaporates, but the graphite prevents any sticking. Threaded holes were cut in the flange and a pair of bolts served to push the pieces apart.

The removable part was provided with unions for supporting the plug and the thermometer. Either thermometer could be used in either place. A hole through this part into the chamber at the base of the plug served as a low pressure lead. Tests in the early part of the work showed that while the air was flowing, the pressure in the flow guide was about 7 cm. of mercury lower than in the larger cross section of flow in the plug just below the flow guide. This is small enough not to be of moment except possibly where the pressure drop is small as well as the flow large, and at low pressure—a combination very seldom used—so that it is sufficient to measure the pressure in the chamber at the base of the plug.

Interchanger.

The air escaping from the porous plug is very near the bath temperature. When this temperature is materially different from room temperature it aids greatly in convenience and cost to use this out-flow air to bring the inflowing compressed air toward the bath temperature. The compressed air was led through a group of 14 copper tubes in parallel, wound into a coil with the turns separated by copper wire, and the return air was led over the outside of this copper tube. The return air at 200° C. gave up so much of its heat to the compressed air, that the returning air escaped from the interchanger at only 10–15° above room temperature. This lessened very greatly the already severe load upon the heating coils and consequently assisted materially in the bath regulation.

Temperature Control.

At the beginning, it was hoped that it would be possible to extend the readings over a considerable range of temperature. Thermostats using volume changes are difficult to extend over any considerable range of temperature, as the filling liquids boil or freeze. If a gas, like air, be used, the sensibility is lowered though the temperature range may be greatly increased, but such thermostats are at best cranky, unreliable pieces of apparatus, requiring continual attention

Thermostatic regulators using electrical properties—resistance or thermal e.m.f.—have been described frequently in the literature.[4, 5] It was attempted to incorporate in one of these electrical control devices the principle of the Gouy regulator.[6]

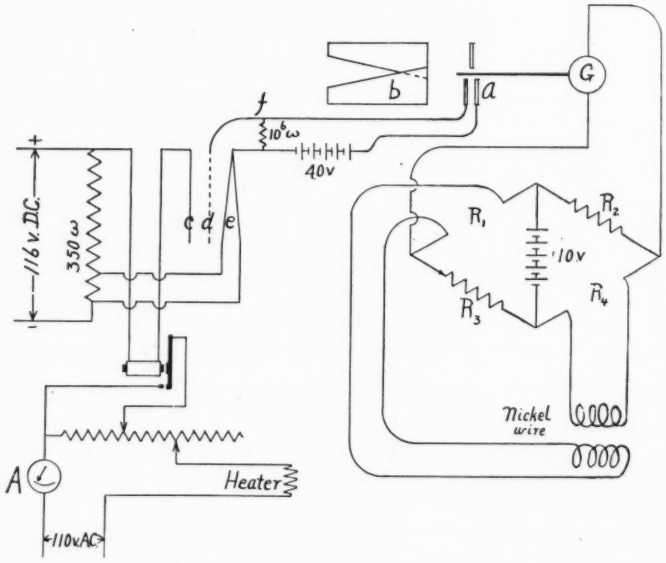

Fig. 2. Arrangement for Temperature Control.

The final form is shown in diagram in Fig. 2. The Wheatstone bridge has arms of about 1000 ohms each and two of its coils R_1 and R_4, are made of very pure nickel wire, 0.003″ in diameter. The nickel wire is some special wire drawn by Driver-Harris Co. from

ingots supplied by M. A. Hunter of Troy, N. Y. If the bridge be undisturbed, the setting will return repeatedly on different days, even around 300° C. to usually within less than 0.1° from the previous setting. It has proved very greatly superior to the copper wire which was used at first.

The first coil is wound on thin mica, the bare wire being carefully spaced, coated with Bakelite lacquer, and baked. The second coil is wound on mica laid over the first, lacquered, baked, and covered with mica for protection. The ends of the coils are lead soldered to terminals insulated with mica, and the leads are insulated with glass tubing. Outside the bath, the leads are very carefully insulated with paraffined glass or hard rubber. This careful insulation improved the regulation very greatly.

The resistance R_2 and R_3 are ordinary resistance boxes having coils of manganin wire with brass blocks and plugs for contacts. Since steadiness during a fixed setting was all that was desired, these proved satisfactory. In regular use, the 110 volt D.C. supply was connected directly across the bridge. When working above room temperature, the energy input from the coils in the bath (about 5 watts) was not objectionable, but it made it more difficult to regulate close to room temperature, and it may easily become serious when the attempt is made to go to very low temperatures.

The galvanometer G is a cheap D'Arsonval type of instrument made for student use. It has an iron core held inside the circular coil. The fields were remagnetized and the coil rewound to lessen the magnetic control. A helical spring was put in to save the upper suspension and a pointer of flattened wire terminating in a short piece of platinum wire was attached to the coil in place of the mirror. A good many more expensive instruments were tried out, but when loaded with this pointer and the auxiliary parts, their sensibility was invariably well below that of this rather crude instrument.

Attached to the front of the galvanometer case were the set of jaws represented in vertical section at a and in front view at b. Both jaws were driven from eccentrics, so that they gripped the platinum pointer without displacing it vertically or disturbing it more than could be avoided. The needle stopped the motion of the jaws till the eccentrics, proceeding with their motion, separated the jaws again. The upper edges of the lower jaws were made of platinum wire, so that the needle made contact between them. The latter were adjusted so that contact was made first at one jaw and then at the other, the second contact bending the flexible needle. Any

sparking on contact took place, therefore, at the second contact and the spring of the needle provided sufficient force to separate them. Sticking of these jaws practically never gave trouble.

Continual trouble was experienced, however, because the touching together of the platinum surfaces failed to make electrical contact. If both contact parts were scraped clean, contact would be made without fail for a few hours, then contact would fail with increasing frequency till the thermostat operation was ruined. Voltages up to 10 volts did not help and higher voltages caused too much arcing. The force across the contact also had very little influence. It is possible that a high frequency discharge in the neighborhood would have helped as with the coherer in the early wireless work. At Professor Terry's suggestion, a three electrode vacuum bulb was set up and the galvanometer contact was used to put a 40 volt stopping potential on the grid. The charge carried across the contacts is only that needed to charge the grid, so that the contacts do not stick from arcing and the 40 volts are sufficient to force the required charge across any contact resistance that has yet appeared. The contact has never been observed to fail though they have not been cleaned for a year at a time.

The details of the wiring are given in the diagram, Fig. 2. The 110 volt D.C. is connected between filament and plate, while the filament is heated by shunting it across part of a resistance which is also carrying the 110 volts. The 40 volt stopping potential is connected between the filament and grid, making the grid negative. When the galvanometer circuit was opened, the charge on the grid took about a second to fall sufficiently to operate the relay. This lag was cut to unobservable size by connecting a resistance of a megohm between filament and grid, and this did not increase the charge moving across the contacts sufficiently to affect the sticking.

The small space current of 5 to 8 milliamperes has to operate the relay. As very large resistance can be used without affecting this current materially, the magnet in the relay was wound with No. 40 enameled copper wire till the resistance was about 20,000 ohms. The moving part of the trip is set on knife edges and balanced carefully, so that it operates rapidly and with great certainty.

The relay is used to lift an iron-tipped copper link out of mercury while an auxiliary contact operates a pilot light. For breaking large currents it is necessary to enclose the contacts in an atmosphere of coal gas.[7] The scheme of the arrangement is shown in Fig. 3. A small gasometer was made of two flat bottom cylindrical glass vessels

and a heavy lubricating oil was used as the sealing liquid. The electrical connections, the gas inlet, and the trip arm were all carried down through the oil and up inside the central vessel. Coal gas was bubbled out through the oil till the air was practically all removed. This cut down the arcing till 32 amperes could be broken every twenty seconds. The mercury did not foul or become pasty, but the whole interior became covered, after many hours of operation, with a gray coat of finely divided mercury.

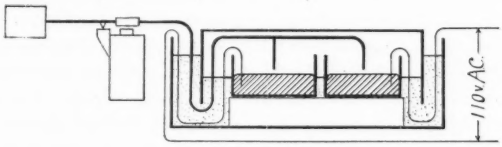

FIG. 3. Trip.

The scheme of the heater control is shown in the lower left of Fig. 2. The heater resistances in the bath were in two groups which could be used in series or parallel. Water cooled resistances, ammeters, and trip were so connected through switches that the heating current could be varied from 0.1 to 65 amperes and the trip could be used to interrupt the whole current or to short any desired part of the external resistance.

With this description in mind, one can go back and discuss the mode of operation of the thermostat. The two jaws shown at *a* and *b*, Fig. 2, approach and recede from each other with a close approximation to simple harmonic motion. The bridge is so adjusted—current and galvanometer—that a rise of temperature of the nickel coils throws the needle to the right. When the jaws are resting on the needle, the stopping grid potential is on, the space current through the tube is stopped and the trip is up. A movement of the needle to the right thus lessens the fraction of the 20 seconds during which the larger heating current is flowing and so allows the bath temperature to fall. With the full sensibility on and a rather carefully adjusted heating current and generally steady conditions, the needle settles down and moves sideways only a few mm. to make the needed continual adjustment. Normally, during a run the heating current requirements lessen slowly, due to the gradual warming up of insulation and outlying parts. The needle consequently tends to drift toward the right, and the necessary rheostat adjustments had to be made occasionally to keep the needle near the middle of its swing. Under

these conditions, a thermometer reading to 0.1° C. with rather large divisions gave usually no indications of change of temperature over hours at a time at any temperature between 25° C. and 250° C., which latter was the upper limit of our set of fine mercury thermometers. In a few instances, the temperature as read on the mercury thermometer drifted slightly after it had had sufficient time to become steady. Such drift was very readily offset by slight adjustments of a slide wire included in the thermostat bridge. This slide wire also facilitated the precise adjustment of the bath temperature to any predetermined temperature. In its final form, which covers most of the data presented here, the thermostat controlled the temperature of a point in the bath well within the requirements set by the other experimental difficulties. This requirement is, of course, made lighter by the rapidity with which the second thermometer T_2 follows the variations of the inlet thermometer T_1. It has the effect of reducing the bath variations as they appear in the observed ΔT and consequently the need for smooth regulation. In the latter part of the work and at 240° to 300° C. the ΔT was read to 0.001° and the last figure has some significance as being the actual ΔT, though the experimental uncertainty in the ΔT, for reasons quite distinct from steadiness of bath temperatures, was very much greater than this.

To save time, the working temperature was reached by use of the 65 amp. current, giving 5 to 12° C. per min. rise, depending on the temperature. On approaching the working temperature, the rate of rise was cut gradually to nearly zero, and the thermostat put in control. It normally assumed its duty without any tendency to hunt. This was usually managed by hand regulation, but if the voltage on the bridge was cut from 110 to 20, and the rate of rise was not too violent, the thermostat also took up its duty without hunting. The lack of sensibility as shown by the chance excursions of the bath temperature disappeared as the applied voltage was raised. At the same time, this increase in voltage increased the heating in the nickel wire coils and hence the bath temperature shifted slightly and became steady at a new value.

In most thermostats, as here also, the temperature control is accomplished by making the rate of energy input a very rapid function of the temperature change. To meet variation in energy demand, a change of temperature is required, which may be made small enough, however, to be experimentally negligible. Such high rates give very unstable conditions and hunting becomes very difficult to avoid.

The hand regulation introduces a new principle, in that it allows a wide range of energy input without a corresponding temperature shift. When so supplemented, a relatively insensitive thermostat may be used. This hand regulation may readily be made automatic by utilizing the inequality in the on and off periods to shift a rheostat in the heater circuit, to bring them back toward equality. This would take care of slow variations in the energy demand, while the on and off arrangement takes care of rapid adjustment. It would be possible to rely entirely on this inequality for regulation, but when so used it would probably set up long period hunting. An apparatus for making this automatic was designed and working drawings made some years ago, the desire at that time being mainly to improve the constancy of temperature. As this end was gained by the use of nickel wire and good insulation, it was not built. It offers possibilities, however, in the control of refrigeration in the low temperature range, and it may become advisable to build it.

Thermometers.

The temperature of the thermostat bath was set and followed by the use of two groups of mercury-in-glass thermometers. One group running from 0–200° C. was made up of low priced bath thermometers. The other group running from 0–250° C. was made up of very fine, "normal" instruments. All read to 0.1° C. They were not depended upon except as indicating instruments. Routine work gave occasional chances for comparison with the platinum thermometers and these mercury instruments proved unexpectedly reliable. For work above 250° the only available indicating instrument was an ordinary 0–360° mercury-in-glass thermometer graduated to 1° C. This merely reduced the convenience of control and does not affect the data.

The temperature measurements reported were all made on platinum resistance thermometers of fundamental interval of about 27 ohms. They were inherited from the porous plug work on water[3] and were much more sensitive instruments than required for the present problem. Accidents happening occasionally made it impossible to take all the readings with one pair of thermometers and they were rebuilt as became necessary. The purest obtainable platinum wire, 0.05 mm. diameter, is supported as nearly strain-free as possible on a mica spindle. The details of the construction have been described in another article.[8] The resistance was read by connecting them through

a general mercury-cup commutator to an equal arm Wheatstone Bridge of the regular Callendar-Griffiths type. The box has been described in detail in the article on water.[3] The passage of the mercury through and over the copper cups forced the rebuilding of the coils and their connections. A mercury-lubricated plug connection was set up as described in another article.[9] The coils are supported from the ends of the copper bars, and are made of manganin, supported strain-free and enclosed in separate containers with kerosene oil. The coils have been calibrated repeatedly since construction, and both errors and variations are far within the limits needed.

The galvanometer is a D'Arsonval type used with 2.5 meters light arm, and its sensibility at this distance is about 10^{-9}. It is read by a light spot on a translucent scale.

It is customary to arrange these bridges with the slide wire contact in the galvanometer circuit. This introduces two serious difficulties, namely, the contacts even when made of the same metal and immersed in kerosene, disturb the galvanometer erratically when the contact is shifted; and, secondly, when the bridge is near balance a very slight non-conducting film will stop the current passing, simulating a balance. This condition can be recognized, but it takes time and careful attention.

On the other hand, the bridge condition is just as well satisfied with the slide wire contact in the battery circuit. The objection to it has been that the sparking at the contact will ruin the slide wire. If the contacts are under kerosene this sparking is greatly reduced, and such circuits are largely non-inductive. Small shifts may be made without separating the wires, and for large shifts the battery circuit may be broken elsewhere. This making and breaking of the battery circuit does not disturb the galvanometer if the bridge is in balance and the contact thermal e.m.fs. merely add themselves to the battery potential. With this arrangement the light spot follows the slider shift almost like a direct mechanical connection, and the balance may be very readily obtained and kept. The final balance is made by reversing the battery potential.

In the use of such sensitive bridges, it is a very great convenience to be able to control the sensibility while making preliminary trials for balance. Any shunts or series resistances in the galvanometer circuit always introduce troublesome thermals, and the necessary adjustments of the sensibility change these thermals. The desired sensibility variation may, however, be very readily accomplished by the use of a sliding arm rheostat to vary the potential applied to the

bridge by means of a group of series and shunt resistances. A combination of this kind can be readily made which will control the sensibility so that in use the light spot may never be thrown off the scale. In this work, where many things called for more or less continuous attention, the time saved by this little device was very important.

The fundamental intervals of the thermometers were determined in the usual steam and ice baths. Check determinations at different times agree to 0.01%. The sulphur boiling point gave 1.49 for the delta of the wire.

Compressor.

The compressor is a two-stage water lubricated machine of 30 ft.^{3}/min. calculated capacity, and of 120 r.p.m. speed. It was exceedingly badly designed and as badly constructed. It has been continually repaired and rebuilt with a regular improvement in its steadiness of delivery. This erratic variation in the delivery has been a source of constant difficulty in the pressure regulation. The details of the compressor history are too rich and varied to be attempted here.

The output of air at high pressure passed through coils of copper tubing immersed in water for cooling, through a trap to separate the liquid water which was fed in for lubrication, and finally over solid stick potassium hydrate or sodium hydrate to take out the water vapor and the carbon dioxide. The same purifier is used for the liquid air work and the clearness of the liquid air, as well as freedom of the valve from clogging, shows that this purification is reasonably effective. The substitution of castor oil for the mineral oil used to lubricate the piston rod packing abolished the appearance of oil in the liquefier.

Pressure Regulation—Barostat.

The control of pressure is a very vital element in this work. Not only is it necessary for the pressure to be steady in order to measure it satisfactorily, but variation of pressure results in corresponding variation of temperature throughout the mass of the gas, even that which has passed the temperature equalizing coils and is immediately around the inlet thermometer. Small pressure changes are thus recorded very rapidly on the inlet thermometer and on the differential reading. Shifts in bath temperature of similar magnitude show much more slowly on the inlet thermometer and still more slowly on the differential reading. It is not at all difficult to estimate the performance of the pressure regulator by observing the movements of the galvanometer in the thermometer bridge circuit.

Moreover, such a sudden shift of pressure changes the heat content of the material in the plug chamber, which has then to be restored by the air flow. This much slower adjustment is likely to be only partly completed when the pressure shifts in the reverse direction and the adjustment must begin over again. Practically all the experimenters since Joule's time have referred to the difficulty from slow drifts. The matter may be well illustrated by reference to the points taken early in the work for the 50° curve of Fig. 8, as compared with those of the 25° curve taken lately. The major difference is due to the pressure regulation.

The pressure of a moving fluid may be controlled in one of two ways, i.e., by controlling the supply or by wasting an excess. The former was used very successfully in the work on water[3] already referred to. Naturally it was tried out determinedly here, but has been abandoned because of (1) the difficulty of speed control of a 25 H.P. motor; (2) the small effect of speed changes on the delivery, due probably to incomplete filling of the first stage cylinder; (3) the capacity in the stages introducing a large lag, so that these regulators hunted violently. A reasonably steady compressor might have made some of these arrangements usable.

The method used in taking all the data recorded here used a spill valve to waste the excess compressed air while the compressor was run as steadily as possible.

Fig. 4 represents, in a diagrammatic way, the arrangement used. *ab* is a steel cylinder which is entered through a leather packing by a steel cylindrical shaft *cd*. The lower section of this shaft where it enters the stuffing box is of hard steel, ground and polished to a very true cylinder, close to ½-inch in diameter. The cylinder *ab* is connected through a heavy steel tube to another cylinder, the two serving as a U tube to hold mercury which transmits the pressure entering at *e* to the castor oil above the mercury in *ab*. If the air was allowed to come directly in contact with the piston, the stuffing box lacked lubrication and had to be kept much tighter to prevent the air escaping than to prevent the oil. The air under the high pressure dissolves sufficiently in the oil to spray it all through the system when the pressure is reduced. A tube leading through a valve to an oil reservoir *F*, allowed the mercury levels to be equalized when there was no pressure on the system.

The shaft *cd* is kept rotating slowly by a belt driven from a cylindrical pulley, so that the belt produces very little axial force on the piston and it is only necessary that what axial force there is should

remain constant. The piston *cd* is loaded by carrying a tank of galvanized iron hung on a vertical shaft through a ball bearing and

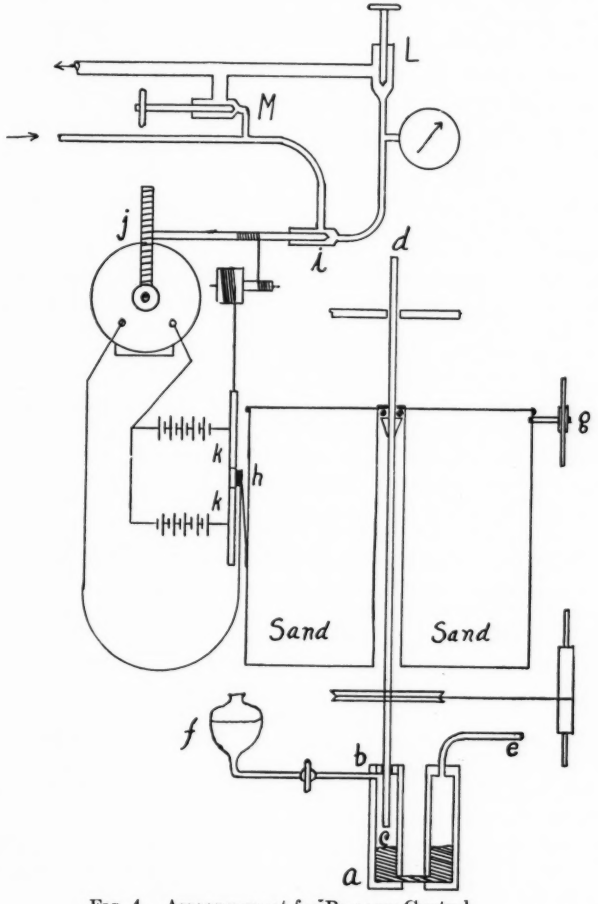

FIG. 4. Arraangement for Pressure Control.

gimbals, so that the load of sand does not rotate and its center of gravity is continually in the axis of the shaft. The tank is kept from

rotating by an arm *g* carrying a wheel set between vertical rails. The cylinder and shaft were set carefully vertical. The whole is supported by a pair of pillars held between ceiling and floor, which also supports the electrical control mechanism represented in the upper left of the figure.

A contact block of graphite, *h*, carried by the load tank is connected by a hanging wire to one terminal of the 20 volt, D.C. motor. The two pieces of copper *kk* against which *h* slides are separated by a piece of porcelain, and are each connected through a battery to the second armature terminal. The field of the motor is separately excited so that when *h* touches the upper strip *k*, the motor operates so as to open the valve *i* by the worm gear *j;* and conversely, when *h* touches the lower strip. The two strips *kk* are carried on a frame suspended between vertical guides and supported by a cord which in some cases was wound directly on the shaft of the valve *i;* more generally it went through a multiplying arrangement by which the proportion between shift of *kk* and rotation of the valve could be changed.

Suppose the delivery of the compressor is too large. *cd* rises, carrying *h* into contact with the upper strip *k*. This operates the motor so as to open the valve *i* and to wind up the cord raising the copper strips till the contact *h* goes back on the procelain; conversely, if the compressor delivery is too small. That is, each vertical position of the piston *cd* corresponds to a particular opening of the valve *i*, and therefore a certain amount of waste of compressed air. If the pressure is raised slowly, the piston rises slowly till an equilibrium state is reached and floats at the level required to waste the excess of air being pumped. If, however, the pressure is raised rapidly near the equilibrium pressure, then the lag of the control, due mainly to the inertia of the load, allows the pressure to rise much above the equilibrium pressure, the piston rises to the limit of its path and the waste valve opens to the limit set for it. The waste is therefore large and the pressure falls again rapidly; the piston falls to the lower end of its path and the cycle is repeated indefinitely. It is necessary, therefore, in order to get steady conditions, to approach the equilibrium slowly. This is arranged very readily by using an auxiliary spill valve *M* to waste almost sufficient to take care of the excess when close to the equilibrium pressure. A little practice allows one to get a steady pressure in a few minutes and this is maintained unless some large abrupt change practically reproduces the initial conditions.

At the high pressure it is difficult to get the waste valve *i* adjusted

to waste little enough. A very small opening allows a very large quantity of air at 200 atmospheres to escape. To reduce the effect of this too rapid opening, the valve L was placed in series with the valve i and a gauge was connected with the space between. This arrangement gave complete and ready control of the amount wasted through i.

The condition of violent hunting described above arose with all of the arrangements tried, but if the irregularity to be smoothed out was not too large, and the regulator was put in control of only a fraction of the flow sufficient to cover these irregularities and the equilibrium state was set up by some manual assistance, then the piston moved slowly back and forth as required by the irregularities of delivery of the compressor and the pressure regulation became reasonably good. It was greatly improved by the changes in the compressor noted above and also by floating on the line four carbon dioxide cylinders. The effect of this volume capacity was to reduce the pressure variation of a given change in the pump delivery, and so lengthen the period as well as lessen the amplitude of the hunting. These improvements made possible the reading of the temperature difference as shown later to 0.001° C. When it is considered that a 1% variation in the pressure at 250° C. would lead to an adiabatic change of temperature of the air of 1.5° C., it is evident that the pressure variation must have been very slow and very small.

Some considerations advanced by W. Trinks[10] made it appear probable that increasing the stability of the moving piston would improve the regulation. A number of screen-door coiled springs were stretched between the load and the supports above. Hence, as the piston rose, the tension on the springs lessened and the pressure had to increase to support the load. One of these springs was found sufficient to decrease the vertical excursions till they were hardly observable. At the same time, the period fell to 15 to 25 seconds without the four cylinder capacity on the line. This made possible the observation with the thermometers of sufficient of these cycles to fix the average position of balance with great certainty. The only data taken with this arrangement is that for the 25° C. curve of Fig. 8. These are the most consistent data yet obtained, and both from this and from the ease of control, this appears much the best arrangement yet tried.

With regard to this pressure regulator, it may be noted (1) the sensitivity, that is, the ratio of shift of position to shift of pressure, may be set anywhere desired between nearly infinite to values lower than ever desired. On account of the inertia of the load, the pressure

shifts during the shift of the regulator, but this persists only during the shift and in the absence of the springs every vertical position of the piston has the same balancing pressure (within the limits of constancy of piston cross section). (2) The energy required to operate the control is drawn almost exclusively from an outside source. (3) Its setting is very steady, that is, what can be called its zero variation is very small. It is of the same order of magnitude as for the rotating piston used to measure the pressure. Consequently, no continual attempt was made to check the steadiness of the pressure by measuring it. Experience has shown that if the piston is holding steady in vertical position, the pressure variation from hour to hour is too small to be measured by any of the ordinary pressure measuring devices save, perhaps, a mercury column. (4) It has a large time lag. (5) It requires a considerable shift in the pressure to shift the piston and load quickly, so that it is not well adapted to take care of large and rapid variation in delivery. The necessity for keeping the load within manageable dimensions restricts the cross section of the steel piston, which limits the obvious way of improving the control over large rapid variations by increasing the volume displacement.

Measurement of Pressure—Manometer.

On account of a series of difficulties, spring gauges are not reliable for careful work, although they are very convenient indicating instruments. Two 3000 lb. Schaffer and Budenberg test gauges of 10″ and 12″ diameter were connected to the low and high pressure spaces during the last part of the work. During most of the work the 12″ gauge could be connected through valves to either high or low pressure. In addition a gauge reading to 50 pounds could be connected to the low pressure so that the difference from atmospheric could be followed closely. While the gauge readings were recorded, as a rule, none are reported. They were used only as indicating instruments to maintain continuous and thorough control over the situation.

The instrument used for measuring the pressure is a modified "dead weight tester,"[11, 12, 13] or free-piston manometer. It was described in detail[14] in an earlier article. Very briefly, it consists of two vertical pistons on the same shaft, one entering a cylinder above and the other one below. The larger pressure was admitted to the lower cylinder and the lower pressure to the upper cylinder and the difference counterpoised by suitable weights. The pistons were

rotated slowly while the load did not rotate. The pressure is transmitted through mercury to castor oil in each cylinder. The pistons and connected parts were counterpoised by a weight carrying an iron cylinder which dipped in mercury and served to give the system an equilibrium position. It was always read by adjusting the weights till the pointer set itself at this zero position.

One change was made from the form described in 1913. Then the rotating pistons were driven by cords passing over a grooved pulley on the pistons and over cylinders set parallel with the piston axis. It required frequent adjustment to keep these axes parallel on account of the stretching of the driving cords due to the spring tension. Mr. Burnett pointed out that if the cylinder were on the piston axis and the grooved pulleys in the place of the cylinders, that this adjustment would be continuous and automatic. There was just room enough to make the change. The zero of the cylinders has not shifted since.

The set of weights used were calibrated as described in the previous article by comparing with the State of Wisconsin sub-standards. The diameter of the piston is taken as the value obtained at that time which gave a check to about 0.1 per cent when both this instrument and the open tube mercury manometer were used to measure a pressure of about 34 atmospheres. Most of the readings are of the difference of pressure across the plug, but the high pressure was also read by opening the upper cylinder to the atmosphere. These high pressure readings require, therefore, an addition of one atmosphere to give the actual pressure. This addition has been made in the data reported here.

Flow Meter.

The ΔT measured does not depend directly on the amount of air passing the plug. Possible corrections, however, do depend upon it and control of the experiments is greatly facilitated by such information. A steel block was bored out, tapering both ways to a $\frac{5}{8}''$ diameter throat from the $1''$ diameter steel tube in which it was mounted and which carried the air from the interchanger back to the compressor. Small holes were bored through the wall at the throat and at the normal size. A ring about the tube at each place served as collector to carry the pressure to a U tube containing water. This meter was calibrated against a good wet gas meter. It was observed, late in the work, that the zero shifted slightly when the compressor was running, even if no air was passing through the apparatus, so

that very small readings are particularly unreliable. No particular attention was given to its study, as it appeared quite secondary to the main problem.

Plug.

The plug used throughout is the radial flow type whose desirable features were described by Burnett and Roebuck,[15] and used later by Roebuck,[3] by Trueblood,[16] by Hoxton,[1] and by Burnett.[2] This plug is a round ended tube of porous porcelain whose length is several times its diameter. Those used were 7½″ long, 1½″ outside diameter, and either 1″ or 1¼″ inside diameter. The edge and about ½″ of the side at the open end were scored in a few places with a file, then rubbed with graphite and a smooth layer of copper half a millimeter thick, plated on the graphite. The copper was lead soldered into a steel collar which was held in place by a hollow nut against a lead or copper gasket. This allowed of ready interchange of plugs and gave no observable trouble from leakage.

The general theory of such a porous plug has been discussed by the authors cited above. In this special case, the external surface can exchange heat only with the fibrous filling of the chamber or with the approaching air. This fibrous packing blocks radiation, being opaque to the effective wave-lengths, and stops convection for even the slow flows, while it makes a trifling addition to the exchange by conduction. The air passing through the plug near its base is led away directly without approaching the thermometer, thus protecting the thermometer from conduction gain from the plug supports. For the major part of the work presented here, the temperature inside the plug is lower than that outside. The directions of the heat flow and of the air flow are therefore alike. Since the drop in pressure is accompanied by a proportionate increase in volume (adiabatic), and the same amount of air must pass every cross section of the flow, it follows that the major part of the pressure drop occurs near the inner surface of the plug wall. If the plug and air had absolutely no heat conductivity, the temperature distribution could be determined from the properties of the air, and the temperature gradient would be much greater near the inner surface. The effect of the conductivity of the air and the procelain will be to move heat forward in the direction of flow. The oncoming air thus drops in temperature faster than called for by its expansion, and its thermal capacity at each point supplies heat for forward conductivity. This limits the fall in temperature of the outer wall which, on account of the smaller pressure gradient in the

outer layers, is thus less than might be expected. The disturbance, by the conductivity, of the air-fixed gradient will therefore depend on the heat capacity of the air passing through, being least with the large flows.

The outer surface of the plug is consequently at a lower temperature than either the walls of the enclosure or the fibrous packing or the approaching air. The temperature gradient in the plug wall may therefore be expected to extend out into the fibrous material. Here the heat flow is not parallel to the gas flow because the gas flow has a component directed toward the base of the plug. The result is that heat is transferred across the gas stream, the air entering near the top of the plug acquiring heat at the expense of that entering later. The very poor conductivity of the fibrous packing and the support of the temperature by the heat capacity of the passing air will reduce the temperature gradient rapidly as distance from the plug surface increases. The limit of the guard ring thus appears to be a compromise between guarding against heat gains from the plug support and loss of heat from air being used to air being discarded. Obviously, only a small portion of the air should go through the guard ring; 1/6 to 1/7 was adopted, but allowance must be made for possible uncertainty in the permeability of the wall.

The permeability of the plugs has offered considerable difficulty. The usual fine grained unglazed porcelain is much too permeable for pressures like those used here. The earlier work was all done with plugs whose permeability had been reduced by precipitating barium sulphate from solution right in the wall. Unfortunately, this crystalline precipitate blows out steadily and repeated fillings lead to very erratic performance by the plug, the blowing out probably tending to increase relatively any lack of homogeneity. It was found possible to use a wash with sodium silicate solution to fasten the crystalline precipitate in place, as on drying the sodium silicate goes to a glass. The sodium silicate solution itself made a fairly satisfactory filling material. Plugs so filled change their permeability only slowly. During this work, arrangements* were made for obtaining a set of plugs of suitable range of permeability by burning at a series of temperatures. These have been used for some of the readings and since the permeability is permanent and the most uniform obtainable over the surface, they offer by all means the best solution of the plug difficulty. I have to thank the Rumford Fund of the American Academy

* Montgomery Porcelain Products Company, Franklin, Ohio.

for the means for obtaining these plugs, as well as Mr. Montgomery for his interest and care.

Inside of the plug and extending over about 2/3 of its outside total length is a flow guide (see Fig. 1). This is a steel or brass tube tapered on the outside so that the cross section of flow is about proportional to the quantity of air flowing. The return passage around the thermometer has the same cross section, and the air is forced to follow a spiral path by a strip of metal. This arrangement of cross section assures the same velocity at all points, thus excluding temperature differences due to variation in velocity. The flow guide is held in place and made tight at the contact with the procelain at the lower end of the guide, by packing silky asbestos fibre into the ring cut out of the metal as indicated in the drawing.

The return flow guide was used in the work with water already cited.[3] The conditions were much more definite than with the air, since the temperature difference was controlled almost entirely by the pressure difference. The evidence there was unmistakable that the flow guide made the observed temperature difference much less dependent on the rate of flow and other chance circumstances beside raising it several per cent so as to give a very much closer check with the expected value. The discussion above is in close agreement with this experimental result. If the plug be used without any flow guide inside, the flow of air within the plug is smallest close to the rounded top and increases steadily from point to point down the plug. The air which stays longest in the thermometer zone and has most effect therefore in fixing the thermometer temperature is the air which has been subjected to the greatest gain of heat, while the air which has lost most heat (speaking only of exchange between different parts of the flow) does not pass near enough to the thermometer to influence its reading. The ΔT read is consequently too small.

If, however, the return flow guide be used, almost all of the air passes along the whole length of the thermometer under conditions of considerable turbulence, and hence this error largely disappears. Two experiments on this point were quite conclusive. In the first, use was made of a valve built into the steel forging which carries the plug. It gives passage to the air from the base of the chamber housing the plug to the passage through which the air escapes from the inside of the plug. It was intended to be used to keep the air-flow through the apparatus constant by being opened to offset the retardation produced by raising P_2. This would simplify both the pressure and the temperature regulation by maintaining a constant load. The ΔT

was read with this by-pass valve open and the compressor delivery high but only a small proportion going through the plug. Then this by-pass valve was closed and one outside the bath entirely was used to waste the same amount. The ΔT now measured was greater by possibly 10 per cent. Here, of course, the conditions are extreme. This by-pass was consequently never used.

In the second of the experiments, a piece of cord was wound around the plug in a steep spiral. A cylinder of paper was bound on gently over this. The spiral at the lower end of the plug was closed by bringing the turns of the cord together. The space outside the paper cylinder was filled as usual with cotton. With this a reading was made of ΔT. The spiral was then rearranged to make the block in the flow fall at the level of the division of the flow inside the plug. ΔT was read again with this arrangement, with other conditions the same, and the value of ΔT is materially larger.

Plug Chamber.

As a result of a number of experiments, it appeared to be substantially indifferent whether the air passed through guides outside the plug dividing it at the level of the division inside, or whether the flow space about the plug was filled with cotton wadding and the air allowed to choose its own distribution of flow. In all the experiments it is moving slowly enough on the high pressure side within this large chamber that no great turbulence is present and the flow is probably stream line. In Fig. 5 are given the data for a pair of experiments where the two series of points were taken under these two conditions and the rate of flow differed materially also. The lowest point of the second series is obviously an error; the rest of the points all fall on the curve almost within the error of plotting. In consequence, the data here presented were all taken with the space about the plug filled with loose cotton or long fiber silky asbestos.

A number of experiments were carried out to determine the difference in the ΔT with this cotton insulation present or absent. Fig. 6 gives one case where the two sets of points fall indistinguishably on one curve. This was for a large flow with a maximum pressure drop of only 29 atmospheres giving a temperature difference of 5.5°, while the maximum flow was 8.1 L/sec. This gives a relatively small heat gain to distribute through considerable heat capacity and the resulting effect on the temperature is not observable. Also it should be noted this is true for the whole curve. The curvature

is not great, so that in a first approximation the temperature difference can be taken as proportional to the pressure difference. As the lower pressure is raised, the pressure difference becomes smaller and the flow falls off, but not as fast as the pressure difference. In consequence, the relation of the heat gain to the heat capacity passing should result in smaller percentage errors for the smaller ΔT.

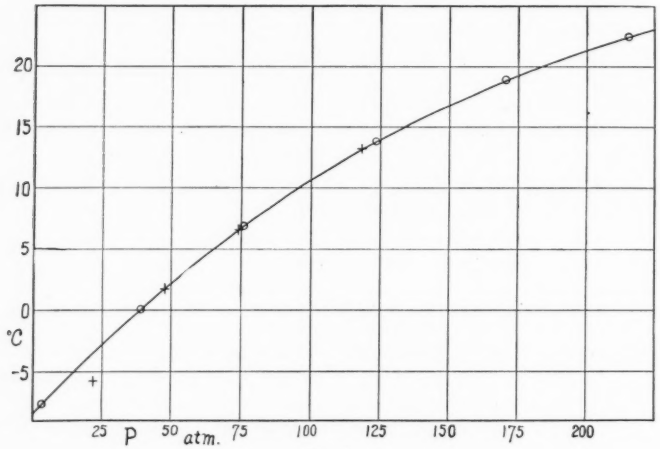

FIG. 5.

The test for an equilibrium condition is that it may be reached from both sides. This second temperature set up by the flowing air should therefore be the same whether approached from a higher or a lower temperature. This was tested repeatedly and in different ways. The set of points forming a curve were determined twice, once with falling and once with rising P_2, as in Fig. 7, Curve A, points ⊙, where the two sets of points all fall on one curve. At another time, the order of taking the points was made erratic without any apparent result on the curve. Again, the point being determined was approached from both sides without any observable difference. This last test served the important practical purpose of proving that the air had been permitted to flow long enough so that the plug interior and its contents had been effectively brought to the temperature of the expanded air. The ordinary proceeding is to follow the ΔT till it becomes stationary but a lingering doubt often remains as to

whether a slow drift will not carry the observed ΔT to a value different enough to be of account. This is answered effectively by approaching the value of ΔT from both sides.

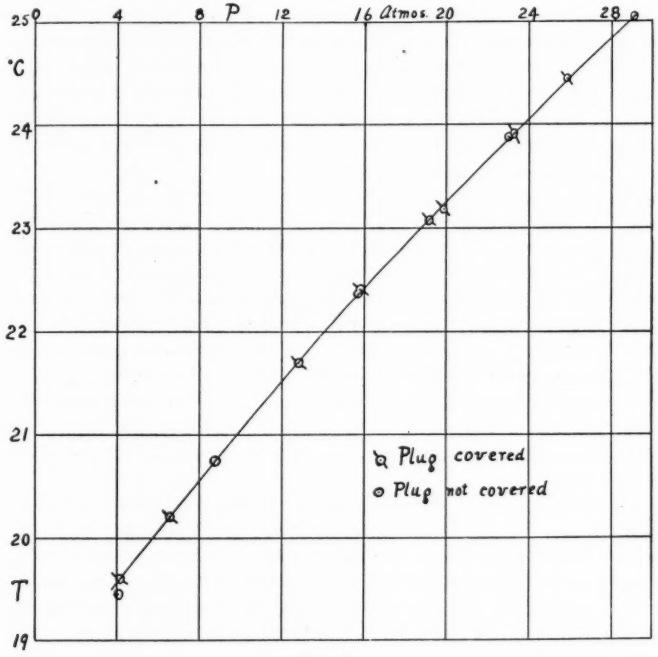

FIG. 6.

KINETIC ENERGY EFFECTS.

Some observers question whether a considerable fraction of the fall in temperature observed in experiments like these may not be due to turbulence which at the time of passing the thermometer has not become fine grained enough to register as heat. If this should be the case, the observed drop of temperature would depend on the time taken for the gas to pass from the plug to the thermometer. The fact that the data reported here are independent of rate of flow rules out this hypothesis of fine persistent turbulence. It is quite possible,

however, that some of the irregularities observed with an occasional plug might have been due to a chance pore being much larger than the average and so giving a streak of violent turbulence which persisted in too large part till past the thermometer. This possibility was tested in one case by comparing the ΔT when the end of the flow guide in the rounded end of the plug was filled with a small wad of cotton, and when not so filled. The ΔT's were closely alike. Had there been any material gross turbulence present, this cotton would certainly have diminished it greatly. Its absence in this case and the general agreement of different plugs makes its presence generally as a material factor very improbable.

The question of the effect on ΔT of the different velocities of flow past the two thermometers has proved a very difficult one, although only of moment where P_2 is less than 10 atm. It is, of course, not difficult to calculate the linear velocity of the air past each thermometer, since the necessary data are readily obtained. But the linear velocity gives no clue to the turbulence of the gross kind which similarly lacks effect on the temperature of the stationary thermometer. This appears quite unamenable to calculation. The velocity past the first thermometer is in all cases too small to affect the temperature appreciably and the same is undoubtedly true of the turbulence. The real problem centers about the conditions surrounding the second thermometer.

The question was attacked from the experimental side in a number of ways. In the preliminary work, where the effort was at first to obtain consistent results, the low pressure P_2 was set at close to atmospheric. That is, the air was allowed to escape from the plug interior with only the rise above atmospheric pressure necessary to force it through the passages. Under these conditions, the velocity past the second thermometer was the largest obtainable and was dependent directly on the quantity of air passing the plug, that is, on the latter's permeability. On account of this high velocity, the ΔT was sensitive to variations in the rate of flow which, not being at first realized, led to much work. When it was realized, the effort to compare individual ΔT's was abandoned, and the regular series of points for each case was taken and the curves compared. This led quickly to very consistent comparisons and to the conclusion that the low end of the curve is its most uncertain region. It is evident also that it is only the low end of the curve about which there is any uncertainty from this cause.

Since the kinetic energy of the air and the turbulence vary some-

TABLE I.

No.	p (atm)	t °C.	Flow L/min.	Plug No.
A 1	4.20	19.59	8.1	1
2	6.59	20.27	7.9	
3	9.21	20.89	7.5	
4	12.87	21.69	6.8	
5	15.84	22.35	6.0	
6	19.93	23.22	4.9	
7	23.27	23.93	3.9	
8	23.34	23.92	3.7	
9	25.89	24.43	3.5	
10	19.33	23.09	5.0	
11	16.36	22.46	5.8	
12	29.07	25.04		1
B 1	4.21	19.64	5.1	2
2	3.20	19.33	5.1	
3	8.91	20.76	5.0	
4	15.65	22.27	4.5	
5	29.07	25.04		
C 1	4.19	19.64	5.1	2
2	21.73	23.68	3.8	
3	14.28	21.94	4.6	
4	29.07	25.04		
D 1	18.07	22.86	9.7	3
2	23.76	24.05	5.8	
3	29.07	25.05		
E 1	3.95	19.60	7.7	4
2	8.36	20.70	7.4	
3	12.53	21.62	6.7	
4	17.66	22.72	5.7	
5	23.12	23.87	4.2	
6	29.07	25.04		
F 1	4.20	19.82	4.3	1
2	2.97	19.45	4.3	
3	6.43	20.35	4.1	
4	9.52	21.04	3.8	
5	18.04	22.84		
G 1	4.19	19.84	3.5	1
2	3.32	19.62	3.5	
3	2.85	19.47	3.5	
4	5.72	20.21		

TABLE I.—*Continued.*

No.	p (atm)	t °C.	Flow L/min.	Plug No.
5	7.28	20.80	3.4	
6	12.21	21.58	3.4	
7	14.32	22.04		

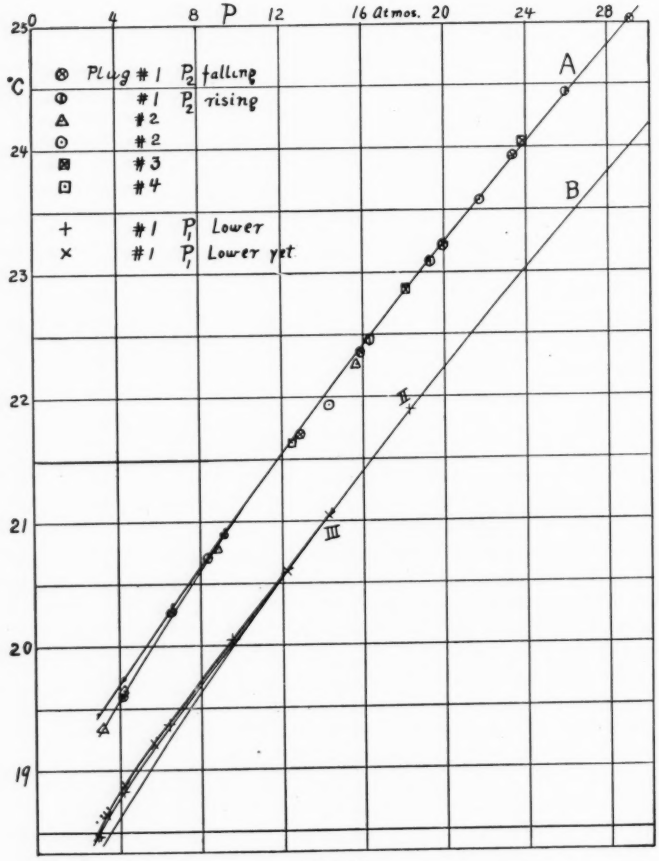

FIG. 7.

what similarly, it was next attempted to plot a series of curves for decreasing velocities of flow, expecting that as the kinetic energy falls with the square of the velocity, the slower flows would have a negligible kinetic energy effect on the ΔT and the curves would become coincident. In Fig. 7, Curve A is a set of points distinguished according to the legend there. The data are given in Table 1. They were taken with four different plugs over which the flow varied by more than a factor of two. The plot is to a large temperature scale and the divergence of the experimental points from the curve is in only one case 0.1° and all the others less than 0.05. The point at 4 atmospheres was taken in all four runs and they fall so close together that only two of them are plotted—and this in spite of the twofold variation of velocity of flow.

At the low pressure end of curve A the kinetic energy corrections for the directed velocity were calculated and this gave the slightly raised line diverging from the original curve at 10–12 atmospheres. The corrected curve loses the sharp bend down and now maintains about the same curvature.

Curve B is curve A transferred down one degree on the scale. Another set of values of T and P were measured using the values at the point II as the initial conditions and one of the plugs used in taking curve A. The effect of this decrease of the initial pressure operating across the same permeability is to decrease the rate of flow. On account of the increase of volume resulting from this decrease of initial pressure, the mass flow falls off much more than proportional to the decrease of pressure drop. Hence the velocity inside the plug falls off sharply and the kinetic energy correction decreases with the square of the velocity. The temperature difference across the plug decreased nearly in proportion to the decrease in the pressure drop, and if the flow did so also, the effect on ΔT of the heat gains would remain the same and the kinetic energy effect could be estimated. But since the flow falls off more rapidly, one cannot distinguish the decrease of kinetic energy effect and the increasing effect of heat gains. The third curve was measured using the point III B as the initial point and the points are distinguished by appropriate symbols. The envelope so drawn falls a little bit higher than the corrected branch of A. How much of the difference is due to heat gains, making B high, and how much to neglecting turbulence in A, it is impossible to estimate. It is hardly possible, however, that the effect of the turbulence is equal to that of the directed flow, so that the correction remaining

is smaller than the correction just made. This is confirmed by the trend of the envelope B where the directed velocity correction is negligible except for the lowest three points.

In another experiment the cross section of flow past the second thermometer was about ½ filled with a metal strip and the divergence from smooth curvature at the lower end compared with a curve taken without this filling. The correction for the filled case is about twice the other. Another comparison, where the passage around the thermometer was about twice the cross section, shows the corresponding variation in the correction. Both of these observations show that the turbulence is not far from proportional to the other factor; and the other facts above show that it is not very large.

Since the correction is as uncertain as a simple extrapolation of the curve, the correction for the lowest 10 atmospheres has not been computed. The correction is necessary only in a very small part of the field covered and will have to be determined by a lot of careful experimental work. By keeping the same length of plug and increasing the cross-section, the velocity can be reduced while the flow per unit area of surface is not changed, and this can be used to separate the effect of velocity of flow and of heat gains. While the question is interesting and important, it has had to be left incompletely solved in this paper.

Heat Leaks.

The most important heat leak is that to the air between the thermometers. With a uniform bath temperature and air which has reached that temperature, the magnitude of this leak will be largely determined by the ΔT set up across the plug. With a given ΔT, the effect of this leak on the observed ΔT will be inversely proportional to the heat capacity in the passing air. With sufficiently large flows the effect on ΔT may be quite negligible. But as the flow is decreased with the same ΔT a condition must finally arise where the heat gain error will reach undesirable proportions. Some of the preliminary experiments showed such errors amounting to 3 to 4% with unprotected plugs, and give ground for the belief that with the flows and protection finally used these errors are below 1%.

The question was investigated by taking cooling curves. The air was kept flowing till T_2 became steady, when ΔP was reduced rapidly to zero, and the variation of T_2 with time followed for half an hour. The expansion of the air in the system produced a sharp fall in T_2

and T_1 which was recovered from quickly. The plot of T_2 against time gave a good logarithmic curve. The constant for the curve and the estimated heat capacities involved were used to calculate the rate of input of heat during normal use, and this input distributed over the heat capacity, 54 cal/min., going through, gives about a 2% correction. This is a large flow but on the other hand the heat gains for no flow must be much larger than for a flow, as interpreted by the thermometer. Probably the main path for heat to get to the thermometer in the no-flow state is along the thermometer case. During flow the heat coming in along this case is largely, if not entirely, caught up by the passing air and carried out again. This would mean that the 2% correction above is a maximum not often approached in the experiments. This agrees with the observations reported where the observed ΔT is independent of the rate of flow.

All this discussion serves to emphasize the principal condition which must be satisfied by data of this kind. It must be proved to be independent of the rate of flow of gas. A change of plug is the most effective way of varying the flow and also serves to exclude the effect of irregularity in the plugs. Shift of the initial conditions will serve somewhat less satisfactorily to shift the relation of rate of flow and drop of temperature. In the published work preceding this, such a condition has never been seriously considered. This situation should change and in the future all such data should be subject to this most obvious and most fundamental test.

The *procedure in an experiment* may be outlined as follows: With the whole apparatus in place, the temperature is raised as rapidly as possible to close to that desired. Time is saved if the final step to this temperature is made slowly so that the thermostat may be put into service and take up its duty smoothly. The heating current required gradually falls off for some time as the insulation warms up. When the major part of the rapid change is past so that the temperature control becomes satisfactory, the compressor is started and the pressure raised to that desired. By operating different waste valves, the flow may be gradually established, accompanied by the necessary but gradual increase in the heating, without disturbing the thermostat balance materially. P_1 and T_1 are read and the adjustments made for reading ΔP and ΔT. Conditions are held as steady as possible till ΔP and ΔT have been steady for four or five minutes when the settings are recorded along with the flow reading.

The lower pressure is then changed by manipulating the valve in the outflow from the plug and the heating current shifted to match.

With experience, this can be done without upsetting the pressure or temperature balance. ΔT, ΔP, and flow are again read after they become steady. And so on for the rest of the points. The difference of resistance of the thermometers when they are both at the initial temperature is always measured by immersing both thermometers directly in the bath fluid, and always checks closely with the calculated values.

Experimental Results.

The data for the main group of experiments are given in Tables II to IX. The data in each table are grouped in runs, distinguished by the letters. The last reading of the temperature and the pressure in each run is the temperature of the bath and the initial pressure, respectively. The air flow expressed in liters per minute measured at

TABLE II.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	84.8	8.83	8.6	14
2	98.9	11.42	7.7	
3	113.9	13.74	7.2	
4	127.9	15.81		
5	142.4	17.75		
6	154.9	19.30		
7	167.8	20.79		
8	215.2	25.19		
B 1	2.0	—10.01	7.2	18
2	13.1	— 6.97	7.2	
3	28.1	— 3.11		
4	41.7	+ 0.14		
5	55.8	3.31		
6	69.0	6.04		
7	84.6	9.02		
8	99.9	11.68		
9	114.1	13.92		
10	129.4	16.15		
11	142.8	17.90		
12	154.4	19.40		
13	168.5	20.93		
14	181.7	22.31		
15	215.2	25.20		

TABLE III.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	149.1	44.42	5.7	4
2	168.8	46.32	4.9	
3	184.7	47.69	4.0	
4	215.9	50.10		
B 1	123.3	41.90	6.1	3
2	180.1	47.50		
3	197.8	48.89	4.1	
4	215.9	50.10		
C 1	55.3	31.47	6.8	4
2	84.0	36.16	6.1	
3	113.7	40.30	5.2	
4	140.1	43.42	3.9	
5	141.0	43.51	4.1	
6	180.3	47.40		
D 1	1.9	20.68	5.9	4
2	13.1	23.28	5.8	
3	35.2	27.84	5.5	
4	56.3	31.80	5.2	
5	84.5	36.41	4.3	
6	123.1	41.28	2.8	
7	156.0	45.34		
E 1	1.3	20.47	3.5	10
2	6.7	21.66	3.3	
3	21.1	24.67	2.9	
4	34.7	27.52	2.1	10
5	43.2	29.12	8.3	7
6	51.1	30.65		
F 1	1.9	20.95		10
2	12.9	23.25		
3	28.1	26.38		
4	42.3	29.13		
5	55.7	31.45		
6	76.0	34.93		

TABLE IV.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	97.1	65.61	7.2	3
2	133.2	69.24	5.9	

TABLE IV.—*Continued.*

No.	p (atm)	t °C.	L/min.	Plug No.
A 3	149.8	70.69	5.6	
4	178.3	72.88	4.3	
5	193.3	73.83	3.6	
6	215.7	75.25		
B 1	20.5	53.96	9.2	2
2	44.3	57.93	8.8	
3	70.7	61.77	8.2	
4	107.0	66.21	7.0	
5	215.7	75.25		
C 1	28.7	55.68	7.7	4
2	57.4	60.15	7.6	
3	85.0	63.79	7.3	
4	122.3	67.95	6.3	
5	160.3	71.25	4.9	
6	215.8	75.25		
D 1	1.6	51.02	5.8	4
2	8.0	52.28	5.8	
3	24.3	55.08	5.6	
4	63.9	61.04	5.0	
5	92.8	64.86	4.2	
6	115.4	67.46	3.5	
7	156.0	71.20		
E 1	1.8	51.18		10
2	13.2	53.24		
3	27.9	55.65		
4	41.2	57.86		
5	55.9	59.72		
6	76.0	62.60		

TABLE V.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	28.4	84.92	9.2	2
2	63.1	89.12	8.7	
3	106.0	93.43	7.1	
4	140.2	96.25	5.6	
5	165.7	97.97	4.2	
6	197.3	99.65	3.1	
7	215.7	100.8		

TABLE V.—*Continued.*

No.	p (atm)	t °C.	L/min.	Plug No.
B 1	89.9	92.15	6.9	4
2	125.2	95.16	6.0	
3	162.2	97.75	4.7	
4	215.7	100.37		
C 1	1.6	81.21	2.5	4
2	6.2	81.96	2.6	
3	12.9	82.92	2.7	
4	20.4	83.95	2.7	
5	34.8	85.82	2.6	
6	55.6	88.27	2.2	
7	76.8	90.46	1.6	
8	109.4	93.82		
D 1	1.8	80.90	5.9	10
2	13.1	82.74	6.0	
3	28.4	84.83	5.5	
4	41.8	86.57	4.8	
5	55.8	88.25	3.8	
6	76.0	90.35		

TABLE VI.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	1.1	137.52	4.1	4
2	13.0	138.83	4.1	
3	28.8	140.25	4.0	
4	49.4	142.01	3.9	
5	69.5	143.58		
6	90.9	145.05	3.6	
7	114.4	146.50	3.2	
8	137.1	147.72	2.9	
9	155.1	148.54	2.9	
10	176.9	149.45	2.8	
11	187.6	149.84	2.7	
12	215.1	150.71		
B 1	78.9	144.28	8.6	5
2	112.5	146.36	7.5	
3	142.5	147.94	6.2	
4	166.8	149.00	5.1	
5	215.1	150.71		

TABLE VI.—*Continued.*

No.	p (atm)	t °C.	L/min.	Plug No.
C 1	1.8	137.42	5.7	10
2	6.6	137.96	5.6	
3	20.0	139.26	5.5	
4	34.6	140.60	5.0	
5	51.9	142.05	3.9	
6	76.0	143.97		

TABLE VII.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	120.0	200.81	6.9	4
2	146.5	201.56	5.8	
3	162.2	201.94	5.0	
4	177.2	202.19	4.2	
5	189.2	202.34	3.3	
6	215.4	202.96		
B 1	1.8	195.89	4.6	9
2	13.2	196.62		
3	27.9	197.43	4.6	
4	51.3	198.57	4.4	
5	92.1	200.18	4.1	
6	145.9	201.67	3.5	
7	215.4	202.96		
C 1	2.2	195.79	6.9	4
2	4.0	196.02	6.9	
3	7.1	196.25	6.8	
4	14.1	196.70	6.6	
5	28.0	197.47	5.2	
6	52.0	198.57		

TABLE VIII.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	1.9	249.54	5.0	9
2	11.9	249.97		
3	29.5	250.54	4.8	
4	49.0	251.12	4.7	
5	71.2	251.65	4.5	
6	107.9	252.29	4.1	

TABLE VIII.—*Continued.*

No.	p (atm)	t °C.	L/min.	Plug No.
A 7	143.1	252.66	3.5	
8	175.5	252.85	3.1	
9	191.6	252.82	2.9	
10	215.4	253.17		
B 1	19.9	250.03	9.5	4
2	57.0	251.18	8.8	
3	91.9	251.99	7.8	
4	130.9	252.61	6.3	
5	160.8	252.83	5.0	
6	197.6	252.79	3.5	
7	161.9	252.83	4.8	
8	215.4	253.17		
C 1	2.3	249.45	6.5	10
2	7.0	249.99	6.5	
3	14.0	250.23	6.3	
4	24.5	250.60	5.4	
5	52.0	251.18		

TABLE IX.

No.	p (atm)	t °C.	L/min.	Plug No.
A 1	84.1	282.65		4
2	119.1	282.95		
3	145.9	282.98		
4	183.2	282.83		
5	197.2	282.53		
6	205.5	282.35		
7	215.4	282.76		
B 1	2.2	281.83		9
2	39.8	281.87		
3	68.5	282.51		
4	106.4	282.89		
5	215.4	282.76		

atmospheric temperature and pressure, is given in the fourth column while the last column gives the serial number of the plug used to get the data. The data and curves are referred to for convenience by the bath temperature used at the highest initial pressure.

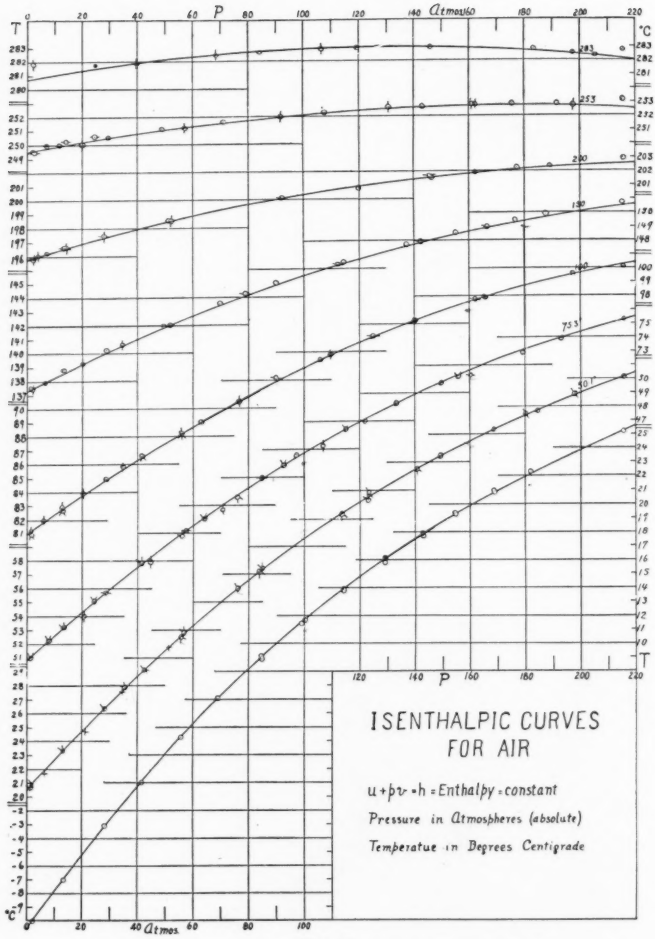

FIG. 8.

This data is plotted in Fig. 8. As far as possible the different points of the different runs are distinguished by different plotting symbols, and the different symbols fall equally well on the curves,

excluding therefore any effect on the data due to rate of flow or particular plug. The curves are plotted with breaks in the temperature scale so that a larger scale may be used in order to emphasize the slope and curvature. The curves are drawn to zero pressure with a steady curvature disregarding a few low pressure points which fall below the curves.

The data were taken in the order from low to high temperature except that the early 25° data had to be discarded, so that the 25° curve shown was measured last. It will be observed, both here and in Fig. 12, that the regularity of the data improves in this same order which is due partly to improvements in the compressor, giving steadier delivery, and to improvements in the pressure regulator, both leading to steadier pressure.

Consideration of the curves shows that with rising temperature they grow rapidly less steep and also decrease somewhat in curvature. The slope $(\Delta T/\Delta p)_h = \mu$ is the Joule-Thomson coefficient, and it is consequently a marked function of both temperature and pressure. The effect of temperature is so marked that it has been observed by all workers, but the effect of pressure has been more in doubt.[2, 18]

$$\text{Locus of Maxima, } \left(\frac{\Delta T}{\Delta p}\right)_h = \mu = 0$$

From the form of all the curves, it appears that this slope must go to zero at sufficiently high pressure on any one curve or at sufficiently high temperature at any pressure. Originally it was intended to limit the work to 250° C., and to 100 atmospheres above 200°. But when it appeared that the maxima were within experimental reach, the range was increased somewhat. The two upper curves show the maximum, and the locus of these maxima therefore cuts across the upper right hand corner of Fig. 8. The location of the maximum on curves showing so little curvature is a matter of considerable difficulty. The graphical treatment can be improved by increasing the temperature scale, but only profitably to a limit set by the consistency of the data. Since the experimental conditions were so very steady it was decided to get these points by special experiments.

The values of P and T for maximum were estimated from these curves and P_1 and T_1 for a curve chosen from a point a few atmospheres to the right of this maximum. Using a very permeable plug so that the flow was large for a small pressure drop, a series of P_2 and T_2's were taken where T_2 covered the maximum. The estimates were near enough that all but one of the four points were obtained on the

first try. The curves formed by plotting the observed ΔT against Δp are given in Fig. 9, from which the pressure for the maximum (marked with a cross) may be read. The corresponding temperature is calculated from the bath temperature and the ΔT. The bath was pushed up to 300° C. which is quite close enough to 327° C., the melt-

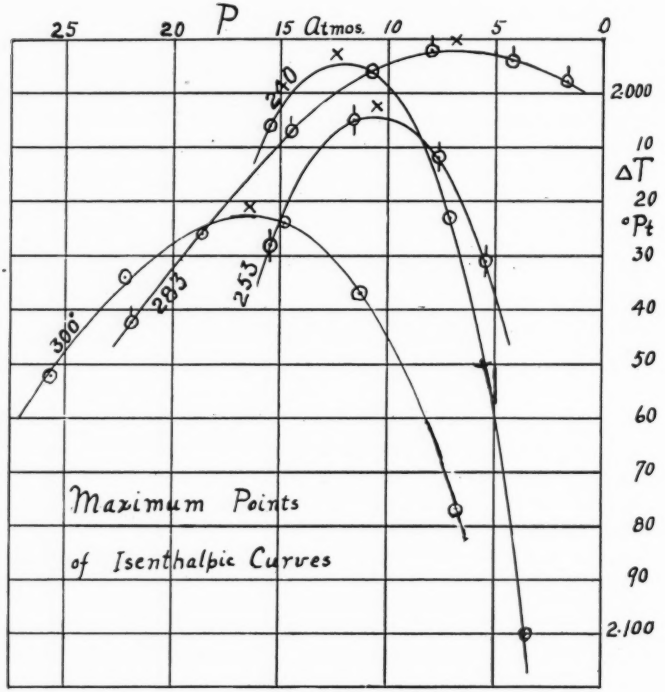

FIG. 9.

ing point of pure lead, which was used to make several joints tight. It will be observed that the curves are consistent to a few thousandths of a degree and P_{max} may be located to about one atmosphere. This shows a remarkably steady state, especially in view of another factor to be discussed later.

The four values so obtained for the shift of the maximum are plotted

as small circles in Fig. 10, while the crosses are from the curves of Fig. 8. It is evident that while the accidental errors in an individual experiment are very low, the systematic errors from one experiment to another are very much larger. The circle at 283° has much the slowest flow, so that the other three circles are probably more reliable. It should be observed, however, that these four special experiments were done only once and without any precautions to show that the results did not depend on the rate of flow.

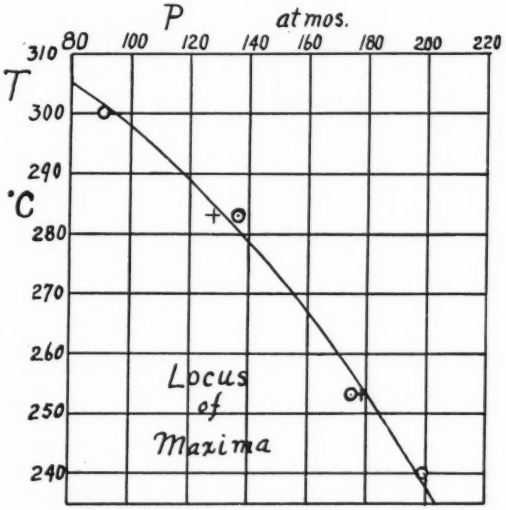

FIG. 10.

The curve of Fig. 10 may be calculated from most equations of state and the comparison of the results with experimental data serves as a peculiarly sensitive test of the equation. Porter[17] and others[18] have carried out such computations for Van der Waals' and Dieterici's equations. Fig. 11 is reproduced here from Noell's article,[18] with the data from Fig. 10 added as circles. To these are added the points lately reported by Knoblauch[19] at — 140° C. at 125 atm. and at — 133° C. at 150 atm. These two groups of points may be connected by a continuous curve somewhat after the manner shown. Both calculated curves are very far from the experimental facts.

Although Dieterici's equation generally gives better correspondence with the properties of the gas, it is the farther off in this case. Noell's extrapolation from his experimental data is also a long way off, which is not surprising in view of the extent of the extrapolation and the uncertainty of the original data. If the extrapolation in Fig. 11 is to be trusted, the whole curve is within experimental reach.

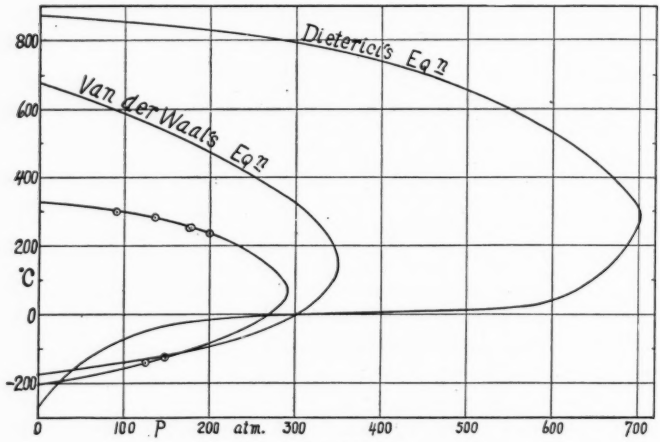

FIG. 11.

Somewhat similar data have been obtained by Olzewski[20] who measured an integrated zero-cooling effect for hydrogen at — 80° C. and under a drop from about 113 to 1 atmosphere, but hydrogen liquefier performance raises some question as to its correctness. Jenkin and Pye[21] observed zero slope for liquid CO_2 for one curve where the observed curves are straight lines.

The most closely related data, however, are in Olzewski's[22] work on the "inversion temperature" for air. In his earlier work, hydrogen at a high pressure was allowed to expand through a valve into a space at 1 atmosphere. An exposed platinum thermometer coil was suspended in the space, and the approaching gas and the space were maintained at the working temperature. Air was apparently treated essentially the same way, except to replace the platinum thermometer by thermocouples. The temperature and pressure were adjusted till the opposed thermocouples in bath and air gave no

deflection, the sensibility being perhaps 0.1° C. In terms of the curves of Fig. 8, if chords be drawn parallel to the pressure axis from the 1 atmosphere point, they will cut the curve again at some higher pressure. What he observed is therefore the zero value of the integral,

$$T_2 - T_1 = \int_{p_2}^{p_1} \mu dp = 0 \qquad \text{where } \mu = f(p, T)$$

This is a different thing from that discussed above, namely $(\Delta T/\Delta p)_h = 0$. His values for P as related to T are reproduced as Table X. From the curves of Fig. 8, the horizontal chord at 283° C.

TABLE X.

Air

P	T
160	+259
100	249
90	244
80	240
70	235
60	226
40	198
20	124

would cut the curve again at about 260 atmospheres. The chord at 300° C. cuts the curve again about 180 atmospheres. From the work presented here, it would appear that Olzewski's values of the temperature for $P = 160$ atm. is at least 50° too low.

Moreover, it is evident from the curves of Fig. 8 that as P is reduced, the temperature at which the horizontal chord runs from 1 atm. to p atmospheres is higher, not lower as he reports (compare Dalton[33]). The form of the whole group of curves makes this necessary and any question of minor errors hardly enters the case.

There are many doubtful points in the experimental arrangements he used. The air escaping from the jet gathers very great velocity and cools itself in proportion. In consequence, it picks up considerable heat from the metal of the valve itself and the walls of the box, so that when the kinetic energy has gone back through gross turbulence to heat, the enthalpy $(u + pv)$ of the gas has increased and the temperature is higher than it should be for the interpretation he puts upon it. This would require that some cooling effect should be left to offset the heat gain and maintain the initial and final temperatures

alike. The observed temperatures for his zero effect would therefore be too low, as seems to be the case.

There is no means of assuring oneself that this kinetic energy has gone entirely back to heat at the time it is in contact with the measuring thermocouple and it seems very doubtful whether it has. If the gas gained no kinetic energy in the valve, the temperature of the expanding gas would first rise and then fall, so that it would be difficult to estimate whether it would gain or lose heat to the valve. The kinetic energy effect is doubtless the dominant source of difficulty, though one would enjoy some experimental proof that the gas actually reached the bath temperature, and as to the bath's uniformity of temperature.

Uniformity of Bath Temperature.

If the group of curves of Fig. 8 are examined, it will be noted that the initial point determined, of course, by the inlet thermometer, falls on the smooth curve up to $T_1 = 75°$. At 100° it is about 0.2° low. At 150° about 0.3° above, about 0.4° at 200°, about 0.5° at 250° and about 0.6° at 283° C. The low end of the curve is separately determined by an experiment with P_1 and T_1 set at values picked from the curve already drawn. These low end curves for 150°, 200°, and 250° showed the same irregularity, that is, the points all fell below the smooth curve already drawn when the initial point was put on this curve. This points to an error in comparing the readings of the thermometers when both are at the same temperature. A number of leads were tried but no experimental work gave any clue till a very porous plug was used, one so porous that the pressure drop is practically zero. This showed a ΔT too large by about 0.7° to 0.8°, which is of the right sign and size to put the low end curves for 200° and 250° on the previous curves. This correction is dependent to not more than 0.08° on the rate of flow but does depend on it. So that it is evident that the temperature of the air changes between the thermometers. At these temperatures the input of energy required to hold the bath at constant temperature ran up to about two kilowatts. It is all put in from the heating coils, Fig. 2, located at one part of the circulation. As an approximation, it was assumed the heat was all added at one point in the circulation, and the rise in temperature calculated. If the oil circulates once per second, this gave about 0.5° C. It circulates fast, but the period is probably nearer 5–10 seconds. In consequence, the air coming from the upper part of the bath is probably above the temperature of the oil about

the plug chamber. The whole base of the apparatus has to be heated from the oil, so the base is necessarily below the temperature of the oil. That is to say, the air will give up heat to the walls of the plug chamber and the observed ΔT will be too large. This agrees exactly with the observation and there is no reasonable doubt but it is the true explanation.

Up to 100° or even 150° its effect on the data is negligible. Also the small influence of rate of flow makes it an almost negligible correction for the other curves except possibly that at 283°. The same holds for the special experiments for fixing the maxima.

This difficulty can be minimized in future work above room temperature, by placing the heating coils on the exterior of the sides and ends of the apparatus, and on the air lead from the interchanger. This latter should be used to bring the air temperature close to that of the bath. The interior coils having very small lag should be used for the control.

There should be pointed out here the definite advantages which this method of obtaining μ, through the isenthalpic curves, has over the differential method used by Joule and Thomson and most of the succeeding workers. This differential method requires that the pressure difference employed be small and consequently also the temperature difference will be small. Any errors in the thermometer zeros, or change of temperature of the air between the thermometers, comes in as a first order effect and is magnified relatively by the small ΔT employed. On the other hand, in the isenthalpic curve method, only one temperature difference among those used depends upon the inlet thermometer. Consequently the effect on μ of any errors in the difference of resistance of the thermometers when both are at the working temperature, does not enter materially in the results. Also if the air gains or loses heat between the thermometers, the total temperature difference so produced does not enter μ, but only its variation between successive readings. From the experimental point of view, these are very material advantages. The isenthalpic curves themselves contain valuable information and while they may be built up by integrating μ (cf. Davis as reported by Keenan[34]), the resulting curves cannot be given the certainty of the directly determined curves.

Joule-Thomson Coefficient μ.

The values of μ may be obtained from this data in a variety of ways. It is necessary always in the reduction of data covering a considerable

field, to introduce arbitrary smoothing somewhere. It was desired to make its introduction and arbitrariness as obvious and reasonable as possible. If one uses graphical methods to get the slopes from the curves, the effect of the process on the results is very difficult to estimate. If equations be written for the curves and the derivatives taken for the slopes, the smoothing is done in part in fitting the equations to the experimental points, and since the slope is the more sensitive function, further smoothing is necessary to make μ consistent over the field. The best procedure appeared to be to calculate μ from successive differences of the numerical data and to draw a set of consistent curves, μ against P, one for each isenthalp. This also allowed of working into the result a lot of fragmentary data, quite reliable but, for various reasons, not suitable for plotting isenthalpic curves. This was done to a large scale and the figure is reproduced here as Fig. 12. The curves were first drawn in as indicated by the points alone. These were then shifted slightly as shown to be advisable by the cross plotting described below, but these small adjustments have still left the curves a fair representation of the data.

It will be noted immediately that beginning with the 50° curve, proceeding down the figure, the consistency of the data improves steadily, with the 25° curve probably the best. Attention should be called to the fact that this successive difference treatment is a very severe test for experimental data. If the values of μ along a curve be used to draw the original isenthalpic curve, it is reproduced usually within the width of the line on the large drawing. The value of μ falls rapidly with both rise of pressure and rise of temperature. Also the curvature as well as the slope of these curves decreases steadily with rising temperature. The same condition holds for these as for the original curves, so that they are also isenthalps.

The curves are carried directly to the zero pressure with steady slope. A number of the points between zero and 10 atmospheres fall well above the curve and are to be attributed probably to kinetic energy effects. Grindley's work[31] with steam indicates that μ keeps its regular value to $\frac{1}{2}$ atm. Gases below 1 or 2 atm. obey Boyle's law very closely, that is, the change of pv with p approaches zero, and hence the contribution of the external work to the temperature change here considered disappears. Depending on the law of force between the molecules, the contribution of the intermolecular work may produce a greater or less fall of temperature on expansion. Any internal molecular contribution is probably very small. So that there

appears no obvious reason for expecting these curves to change their direction suddenly at low pressures.

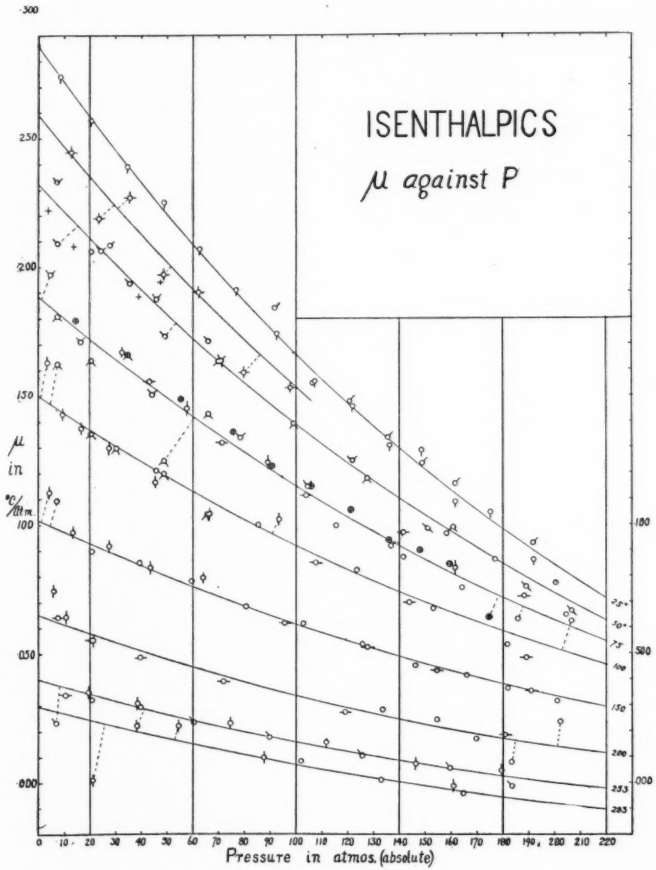

FIG. 12.

The curves of Fig. 12 were next changed to isopiestics by picking off the values of μ for a set of pressures—1, 20, 60, 100, 140, 180, and

220 atm.—and from the original curves picking the temperature corresponding to the μ and p. These values of μ and T are plotted in Fig. 13, and smooth curves—isopiestics—then drawn through the points. The points fall with one or two exceptions (the 100° curve) readily on smooth curves within the error of plotting. These two

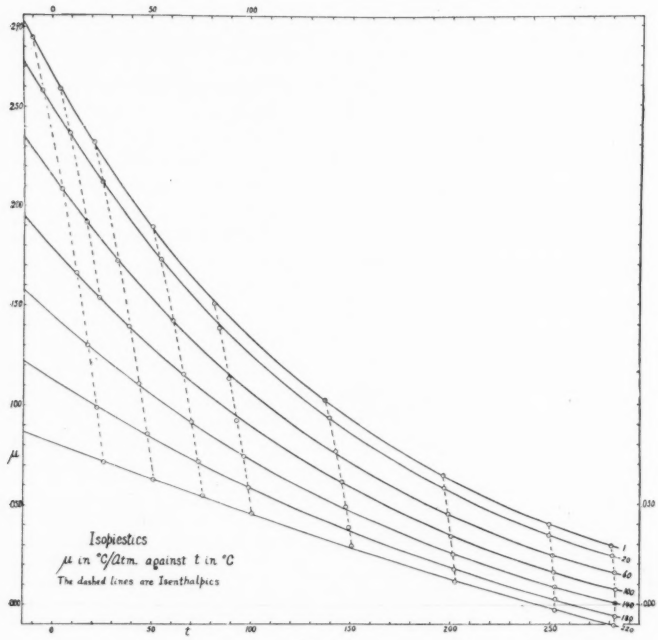

FIG. 13.

groups of data are really independent, so that this excellent fitting of the data into this second set of curves adds confirmation at least to the consistency of the data.

The curvature and slope of the isopiestics of Fig. 13 fall off rapidly with rising pressure, till the 220 atm. isopiestic is almost straight. The values of μ for a group of integral values of p and t were then picked off and are tabulated in Table XI.

TABLE XI.

μ AS A FUNCTION OF T AND p

Press.	0°C.	25	50	75	100	150	200	250	280
1	.2663	.2269	.1887	.1581	.1327	.0927	.0625	.0402	.0297
20	.2494	.2116	.1777	.1490	.1244	.0856	.0564	.0346	.0246
60	.2143	.1815	.1527	.1275	.1057	.0708	.0447	.0251	.0161
100	.1782	.1517	.1283	.1073	0890	.0587	.0347	.0164	.0078
140	.1445	.1237	.1047	.0875	.0723	.0467	.0258	.0093	.0011
180	.1125	.0974	.0833	.0800	.0578	.0366	.0185	.0027	—.0054
220	.0812	.0718	.0627	.0542	.0452	.0286	.0127	—.0020	—.0110

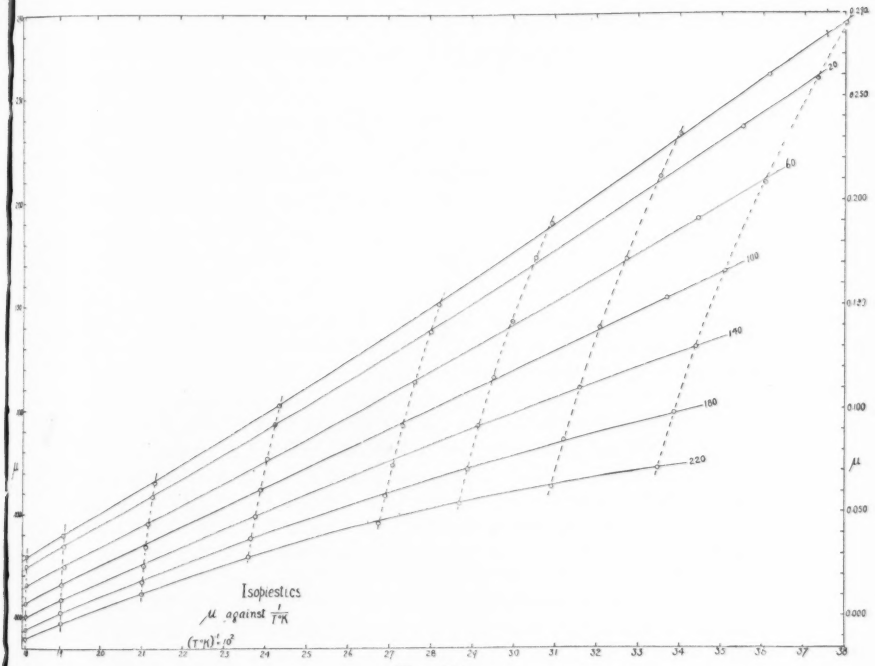

FIG 14.

These isopiestics were next replotted, now however as μ against the reciprocal of the absolute temperature, and this is reproduced in Fig. 14. The 100 atm. isopiestic is a straight line and the other curves

are convex toward it. The curvature of the 1 atm. line is very small, so that the equation proposed by Rose-Innes,[23] by Keyes,[32] and by Buckingham[24] make good approximations at 1 atmosphere. The curvature increases however quite markedly at the higher pressures.

Specific Heat.

The original isenthalpic curves of Fig. 8 are characterized by the condition that $h = (u + pv)$—the intrinsic plus the pressure volume energy—is a constant. If heat energy be added at constant pressure to the gas at a point on one curve to carry it to a point on the next curve, then

$$h_2 - h_1 = \int_{T_1}^{T_2} C'dt = C\Delta T^*$$

The value of C' changes very slowly with pressure, so that for not too large temperature changes, C may be set as the average value of C' for the interval and will approximate very closely to the actual value of C' at $(T_1 + \frac{1}{2}\Delta T)$. Hence, between a given pair of isenthalpics

$$\frac{C_1}{C_2} = \frac{\Delta_2 T}{\Delta_1 T}$$

Hence, if the specific heat C be known at one pressure over the range in temperature, this relation may be used to calculate it over the pressure range covered by the curves.

To use this relation required a long numerical calculation, which may be summarized as follows. The values of T at 10 atm. intervals along the curves of Fig. 8 were calculated, using the values of the slopes picked off the large scale plot (Fig. 12), the values being calculated in two series, one each way from a point about the middle of the curves of Fig. 8. From these the values of ΔT between each pair of curves were obtained, as also the average value of T for each ΔT. The ratio of the ΔT at 1 atm. to the other ΔT's between the same pair of isenthalps, give the factors by which C for 1 atm. is to be multiplied. These factors were then plotted and smoothed, the maximum uncertainty being about 1%, but averaging 0.2 to 0.3%. From these curves were read off the factors used to multiply the C at 1 atm. of Table XII to fill the following columns. These values for C at 1 atm. are taken from the Reichsanstalt Tabellen[25].

* Since C_v is not mentioned, C is used here for C_p.

TABLE XII.

C AS A FUNCTION OF T AND p

Press.	0°C.	25	50	75	100	150	200	250	280
1	.2405	.2410	.2415	.2419	.2424	.2434	.2443	.2453	.2458
20	.2492	.2487	.2480	.2475	.2470	.2466	.2463	.2468	.2471
60	.2656	.2627	.2603	.2581	.2562	.2532	.2512	.2500	.2492
100	.2804	.2760	.2717	.2681	.2650	.2602	.2565	.2536	.2519
140		.2873	.2816	.2767	.2725	.2658	.2607	.2566	.2544
180		.2960	.2898	.2840	.2790	.2707	.2644	.2596	.2569
220		.3020	.2956	.2893	.2838	.2748	.2678	.2622	.2593

C shows a uniform increase with pressure over the range covered but the increase falls rapidly, so that probably it would reverse at still higher temperatures. At one atmosphere C increases with temperature, but at 20 atm. there is a minimum at about 200° C. and at the higher pressures C decreases with rising temperature. The values at 0° C. at the higher pressures could not be obtained without a marked extrapolation and are not recorded.

The Reichsanstalt[25] publishes an equation for the variation of the average C (between 20° and 100° C.) with pressure. This equation was used to calculate C_{60} recorded in Table XIII; while the factors

TABLE XIII.

COMPARISON OF C'S AT 60° C.

Press.	1	20	60	100	140	180	220
Factor	1.0	1.025	1.0725	1.118	1.157	1.189	1.2125
C	0.2419	0.2480	0.2595	0.2705	0.2799	0.2876	0.2933
C_{60}	0.2419	0.2473	0.2590	0.2699	0.2805	0.2884	0.2950
Diff. %	0	+0.28	+0.19	—0.22	—0.21	—0.28	—0.59

and C were calculated as in Table XII, using 0.2419 as the value at 1 atmosphere for both C's. The two values of C show increases with increasing pressure, but C_{60} increases more slowly than C at low pressures and more rapidly at high pressures, till about 0.6% different. The agreement is about what could be expected.

THE PRODUCT, μC

The values of μ of Table XI and of C of Table XII were combined to give Table XIV where μC is tabulated as a function of T and p, since this product is useful for many calculations. The value μC

falls with rising pressure as well as with rising temperature, being controlled by the larger variation in μ.

TABLE XIV.

$\mu C \times 10^2$

Press. Atm.	0°C.	25	50	75	100	150	200	250	280
1	6.404	5.464	4.557	3.825	3.216	2.256	1.527	0.986	0.730
20	6.215	5.261	4.407	3.688	3.073	2.111	1.368	0.854	0.608
60	5.691	4.768	3.975	3.291	2.708	1.785	1.123	0.627	0.404
100	4.997	4.188	3.462	2.877	2.359	1.527	0.890	0.416	0.196
140		3.564	2.949	2.421	1.970	1.241	0.673	0.239	0.028
180		2.883	2.414	2.272	1.612	0.991	0.489	0.070	—0.138
220		2.169	1.853	1.518	1.293	0.786	0.340	—0.052	—0.285

THE ABSOLUTE TEMPERATURE OF THE ICE POINT.

The fundamental thermodynamic equation for the porous plug experiment, namely

$$\mu C = T\left(\frac{dv}{dT}\right)_p - v \qquad (A)$$

may be readily rewritten[24] as

$$\frac{v}{T} - \frac{v_0}{T_0} = \int \frac{C\mu dT}{T^2} = -\int C\mu d\frac{1}{T} \qquad (B)$$

where T is in the absolute scale. For the present purpose, we have $T - T_0 = 100$ and $v = v_0(1 + \alpha\, 100)$ both by definition.

A plot of uC for 1 atm. between 0° and 100° C. shows it to be so nearly a straight line that the difference produces less than 1% in the integral. That is, we may write

$$\mu = A\frac{1}{T} + B$$

and therefore (B) may be written

$$T_0 = \frac{1}{\alpha} + \frac{T_0(T_0 + 100)}{100\,\alpha\, v_0}\left[\frac{A}{2}\left(\frac{1}{T_0^2} - \frac{1}{T^2}\right) + B\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \qquad (C)$$

From Equation C it is evident that the large term on the right is a correction term, since T_0 is approximately equal to $1/\alpha$. This complicated term for air at 1 atm. comes out as less than 1% of T_0, so that the even value 273 may be used for T_0,

$$1/v_0 = 1.293\ g/L \text{ at } 0°\text{ C. and } 76\text{ cm.}$$

and its value must be adjusted by Boyle's Law to suit the pressure under which α is measured. The values of the integral are not materially different at these slightly different pressures. The values so obtained for T_0 are given in Table 15.

TABLE XV

100α	$1/\alpha$	$p(mm)$	Observer[26]	T_0
0.36730	272.26	1000	Chappuis	273.18
0.36732	272.24	1002	"	273.16
0.36708	272.12	760	Eumorfopoulos	273.12
			Average	273.15

The value used by Griffiths[29] is 273.10 and by Henning [26] 273.09. Buckingham picks 273.13 from the data then (1907) available and Keyes[22] (1920) 273.14. Some of the available data is collected in Table XVI for comparison here. Since Keyes' summary the beautifully consistent work of Henning and Heuse[25] has appeared. It should be weighted heavily in comparison with previous work, and the probable value of T_0 may be set at 273.17 ± 0.02.

TABLE XVI.

Observer	Air	H	N	He	CO_2	Method	Date
Berthelot[28]	273.19	273.05			273.10	J-T data	1907
Buckingham[24]	273.27	273.06	273.25		273.12	"	1907
Buckingham[27]	273.27	273.05	273.29		273.27	"	1908
Hoxton[1]	273.35					"	1916
Roebuck	273.15					"	1925
Berthelot		273.07	273.09		273.12	$\alpha_v = \alpha_p$ for $p \doteq 0$	1907
Henning and[35] Heuse		273.17	273.18	273.22		"	1921

In connection with the present work, it is of interest to note that Hoxton's correction is undoubtedly too large as discussed below. Buckingham's value from air is also high on account of Joule-Thomson's data being somewhat higher than that in the present paper. Berthelot's value from air (J-T basis) is much lower than the other workers have obtained from the same data. All these values have been based on Chappuis' value for the average coefficient.

It should be emphasized that not sufficient attention has been paid to the absorption of gas (cf. Keyes[32]) on and in the wall of the container. It is a simple matter to vary the ratio of volume to exposed surface and extrapolate to zero surface, as well as to free the

surface layers from all other gases. The effect of variation in the absorption between 0° and 100° C. will enter differently in the two methods. To assume its effects zero in the $p = 0$ method is hardly justified, though it might be expected to be of less importance. In a comparison of the two methods, this is hardly an advantage, as its effect must be followed to low pressures. In consideration of the greater ease of measuring the coefficient at ordinary pressures, and the small accuracy required of the Joule-Thomson data, this method would seem to be preferable. The meagerness and uncertainty of the available Joule-Thomson data have been much against it, though it now appears as if uncertainty in the coefficient has had a somewhat equal effect on the results.

Coefficient of Expansion.

With $T_0 = 273.15$ as determined above, the equation C may be rewritten as

$$\alpha = \frac{1}{273.15}\left[1 + \frac{273.15 \times 373.15}{100\, v_0}\int \mu C d\frac{1}{T}\right]$$

$$= \frac{1}{273.15}\left[1 + \frac{4.213 \times 10^4 I}{v_0}\right] = \frac{D}{273.15}$$

and used for calculating α, the average coefficient between 0° C. and 100° C., as a function of the pressure. The integral I and specific volume v_0 (Witkowski's data[30]) are both functions of the pressure. These values are collected in Table XVII with the resulting values for α. The fractional part of the factor D is calculated from this data and should be trustworthy to about 1%. The uncertainty in α from this cause only is listed under E. The way that the integral of μC enters the coefficient makes it a very advantageous means for determining α especially for its smaller values, though even at 100 atm. the advantage still amounts to a factor of 5.

TABLE XVII.

Coefficient of Expansion.

p	v_0	$I_p \times 10^5$	D	$E\%$	$\alpha \times 10^3$	$\alpha_1 \times 10^3$	$\alpha_2 \times 10^3$
0	∞		1.0		3.6610		
1	773.4	4.725	1.0025	0.003	3.6704		3.666
20	38.28	4.568	1.0503	0.05	3.845	3.83	3.826
60	12.54	3.869	1.1300	0.1	4.137	4.18	4.166
100	7.49	3.571	1.2009	0.2	4.397	4.41	4.424

For comparison the values of α determined by Witkowski[30] are given under α_1, and by Holborn and Schulze[30] under α_2.

Other Work on μ for Air.

For comparison, Table XVIII gives the previous data over the range of temperature 0°–100° C. at one atmosphere. It will be noted that Hoxton's data are largest, followed in order by Joule-Thomson, Noell, and the author.

TABLE XVIII.

μ from Different Observers.

t °C.	J-T	Noell	Hoxton	Roebuck
0	0.275	0.278	0.303	0.266
50	0.204	0.185	0.226	0.189
100	0.147	0.125	0.170	0.133

Hoxton's[1] data are quite materially higher. In connection with this, it might be pointed out:

(1) That the inlet thermometer in Hoxton's set up is some distance from the plug chamber which gives opportunity for heat transfer to or from the air after it has passed the first thermometer. The velocity of flow of the air and the opportunity for its temperature equalization with the bath were such that this difficulty was probably not of a magnitude to account for the shift of his curves off the zero or for his uniformly large values.

(2) That the carrying of the whole air flow down to the base of the plug by the use of the radiation shield is undoubtedly the main cause of the difficulty. The plug supports are subject to a continual withdrawal of heat by the expanded and cooled escaping air, so that the region about the base of the plug is certain to be somewhat below the bath temperature, and the air, in passing it, loses heat. Changes in the rate of flow affect the expanded air, as well as the approaching air, so that beside the shift of the line off the zero there should also be a shift of slope. The author's experience has been that the ΔT observed is rather surprisingly sensitive to the treatment of the air in the plug chamber. On the basis of this experience, Hoxton's arrangement seems quite sufficient to account for the difficulty.

(3) That uncertainty in the zeros of the thermometers, especially for his very small observed ΔT, may also account for part of the trouble. Reading the differential zero with one thermometer inside

the plug, while the other was inside the inlet tube, places the two thermometers under radically different conditions for equalizing with the bath, both as to the main temperature equilibrium and as to the dissipation of the current heating.

Hoxton's work was greatly superior to preceding work in his careful temperature and pressure regulation, and careful temperature measurement. In the light of my experience, it was unfortunate for his objective that in limiting his problem he chose the much more difficult low pressure part of the field.

Joule and Thomson worked under such different conditions of temperature and pressure regulation, as well as measurement, especially of temperature, that comparison of their pioneer work with work done now is difficult and seems unfair. Outside of these considerations, it was unfortunate that they did not measure the temperature of the air which was entering the plug. One can point out a good many probable sources of error, and it is a great tribute to Joule's experimental genius that his data were correct enough to hold the field for so long.

Noell's[18] work was done under modern conditions, but takes less advantage from it than would be expected. The regulation of both temperature and pressure appears to have been entirely manual and in view of the persistent drifts regularly encountered, this would explain part of the large irregularity in the data. The author's whole experience shows that it is almost impossible to get consistent data without the finest regulation, particularly of the pressure. A slowly rising pressure, for example, adds heat to the air between the thermometers, so cutting down the observed temperature difference, and if this drift of pressure is steady the ΔT is steady. A temperature drift acts similarly, the second thermometer lagging behind the first on account of the heat capacity between them, and if this drift in the bath temperature is steady, the observed ΔT is also steady. Before a steady ΔT can be interpreted as therefore the ΔT desired, it must be known independently that the initial pressure and bath temperature are steady to the limit required by their effect on ΔT. For example, the ΔT in my work was regularly read to 0.01° C. and the bath temperature was held steady over long intervals to 0.01 to 0.02° C.—which is certainly within the requirement. The requirement in the pressure regulation is much more severe experimentally, so that even with the best regulation attained in my work, it was still easily possible to observe the effect of pressure variations actually present, in the rise and fall of ΔT. The best which could be done has been to

make this cyclic variation rapid so that a good average could be taken. The pressure variations in question cannot be observed with certainty on a good test gauge, so that they are quite a different order of magnitude from those present under hand regulation guided by spring gauge indications. Under these latter conditions, it will be quite impossible to tell when the ΔT is free from the effect of pressure variation. The phenomenon is made still more complex by the ΔT being the difference in two temperatures read in connecting chambers, in both of which the pressure must be constant while the second chamber always lags behind the first in pressure changes, as also in temperature changes. When the employed ΔT is made small, as in Noell's work, the effect on μ of these pressure and temperature variations is exaggerated, so that a large variation is to be expected.

The heat leak conditions around the plug are open to strong objection. The conditions of the experiment require that there shall be a temperature gradient between high and low pressure surfaces of the plug. His plug is a wad of asbestos compressed in a steel tube. The air in passing across the asbestos will spread over its whole cross section, the flow being limited all around by the steel tube. This tube will doubtless have a temperature gradient, but that it will be the same as the air flow is hardly possible. The air will probably gain heat from the metal wall, whose temperature is supported somewhat by the flow in the annular space outside. From the diagram it appears as if all of this contaminated air must pass the thermometer, though the text indicates that the double wall of insulator is to divide the flow. It would be better still if the inner insulating tube ran right through the plug and so kept the flows really separated. Noell seems to be concerned only with heat conducted parallel to the direction of flow, though such conductivity cannot affect the ΔT once a steady state has been set up.

For comparison, Fig. 15 gives Noell's data plotted with crosses and circles to keep the series distinct and help relate the points to the companion curve. Noell's curves representing his equations are plotted as dashed lines, and the author's curves as solid lines.

It will be observed first that his curves and points fall together very imperfectly. Any one series of points could be represented very much better by a line drawn through them, but the set of such lines varies so irregularly in both position and direction that they cannot be fitted into any orderly system. The particular system chosen to represent such points is therefore very arbitrary. As a matter of fact, the author's curves represent the points almost as well as Noell's.

This chaotic irregularity is very strong evidence of experimental uncertainty, such as might be expected to result from uncertainty in pressure and temperature regulation. On the other hand, the regularity of any one series and the agreement of single points indicate rather systematic than chaotic errors, such as might arise from heat leaks.

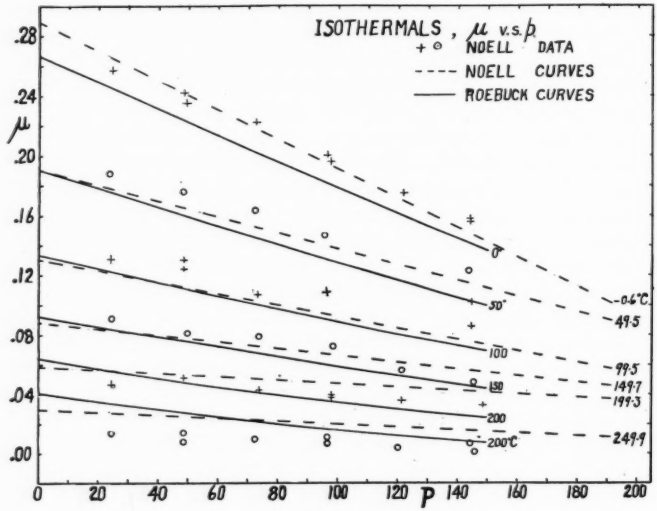

FIG. 15.

CONCLUSION.

The data in this paper cover the readily available temperatures above that of the room. A bath liquid above 300° C. is a serious problem. It also covers the available and useful pressure range. It would be interesting to extend both these ranges to fill in the inversion curve points. But the more profitable field appears to be the low temperature range, and these measurements will be extended as quickly as available time, and to as low a temperature as the available facilities allow. These facilities include a carbon dioxide ice machine and a compressor which may be used for an ethylene cycle, so that it is hoped to get well down into the liquid-vapor region.

Meanwhile, there are also quite a number of related facts which may be extracted from the above data, such as the correction to the Kelvin scale, the volume temperature coefficient of expansion, the free expansion effect, and so forth. Such computations will be carried out and extended to the new data as they become available.

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